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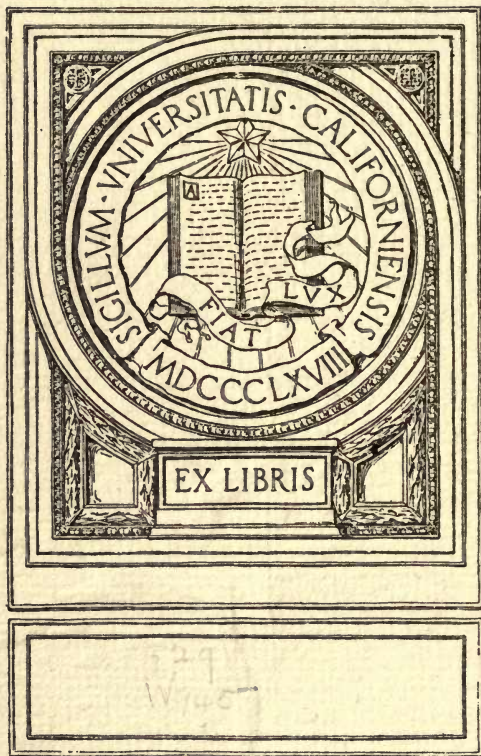
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THE ORGANOMETALLIC COMPOUNDS OF ZINC AND MAGNESIUM

BY

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at the Municipal Technical Institute, Belfast*

EDITOR'S PREFACE

THE progress of Chemistry is so rapid that it is becoming a matter of ever-increasing difficulty to keep abreast of the modern developments of the science. The volume of periodical literature is so enormous that few can hope to read, far less assimilate, all that is published. The preparation of summaries has therefore become a necessity, and has led to the publication of various well-known journals devoted to the abstraction of original papers. For obvious reasons, however, these do not fully supply the wants of advanced students and research workers, and it is now generally recognised that monographs on special subjects are also needed.

This series of monographs is intended primarily for Advanced and Honours students. As each monograph is written by an author with special knowledge of the subject, and copious references are given, it is hoped that the series will prove useful also to those engaged in research.

January 1913.

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The Organometallic Compounds of Zinc and Magnesium

SECTION I.

GRIGNARD'S REACTION—INTRODUCTORY.

IN 1899, Barbier[1] found that when methylheptenone, $(CH_3)_2 . C : CH . CH_2 . CH_2 . CO . CH_3$, was allowed to react with methyl iodide and magnesium in the presence of ether and the product so formed decomposed with dilute acid, dimethylheptenol, $(CH_3)_2 . C : CH . CH_2 . CH_2 . C(OH)(CH_3)_2$, was formed. This observation suggested that the magnesium had reacted with methyl iodide to form magnesium methyl iodide, CH_3MgI, which had then transformed the ketone into an alcohol analogously to the well-known action of zinc alkyls on ketones.

E. Frankland and Wanklyn had previously observed the formation of the compound, $Zn(CH_3)_2 . (C_2H_5)_2O$, when zinc, methyl iodide, and ether were heated in a sealed tube. Starting from these known facts, Grignard[2] was led to investigate the action of magnesium on methyl iodide and similar compounds in the presence of anhydrous ether. Magnesium alkyl halides were thus obtained, which are classed generally under the name " Grignard's Reagents."

The preparation and use of Grignard's reagents are exemplified in the preparation of trimethyl-carbinol from acetone and magnesium methyl iodide. The following description is typical:—

Preparation of the Ethereal Solution of Magnesium Methyl Iodide.—Twenty-five c.c. of a solution of methyl iodide (49 grams) in dry ether (25 c.c.) are allowed to flow on to magnesium (8·2 grams) prepared by cutting clean magnesium ribbon into pieces of 1-2 cms. in length. A brisk reaction commences after a short period. The reaction mixture is cooled with water, two portions of ether (each 100 c.c.) added, followed by the remainder of the methyl iodide solution, the latter being added drop by drop, cooling being adopted if necessary. To complete the reaction, the ethereal solution is heated to gentle boiling during thirty minutes.

Action of Acetone on Magnesium Methyl Iodide Solution.—A solution of acetone (20 grams) in dry ether (20 grams) is added drop by drop to the cooled solution of magnesium methyl iodide. Each drop causes a hissing sound and produces a precipitate which, at first, is redissolved, but subsequently collects as a greenish-grey viscous mass at the bottom of the flask. Reaction is completed by allowing the mixture to remain overnight at the room temperature. The product is decomposed by the addition of ice in small pieces, accompanied by brisk agitation. As soon as the colour of the precipitate is changed to white, sufficient acetic acid (33 per cent.) is added to bring about its

solution. The ethereal and the faintly acid aqueous layers are now separated. To isolate the trimethyl-carbinol—which is present in each layer—the ether is distilled off from the ethereal solution and the residual oil united with the acid aqueous layer and distilled with steam until a sample of the distillate does not become cloudy when saturated with potassium carbonate. The trimethylcarbinol is salted out from the distillate by means of potassium carbonate, dried over solid potassium carbonate, and distilled. To complete the desiccation, the product is left in contact with barium oxide, at first at the room temperature, subsequently at its boiling-point, after which it is again distilled. The reactions involved may be represented by the following equations : —

$$CH_3I + Mg = CH_3 . Mg . I$$

$$\begin{matrix} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{matrix} C = O + CH_3 . Mg . I = \begin{matrix} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{matrix} C \begin{matrix} \diagup OMgI \\ \diagdown CH_3 \end{matrix}$$

$$\begin{matrix} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{matrix} C \begin{matrix} \diagup OMgI \\ \diagdown CH_3 \end{matrix} + H_2O = \begin{matrix} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{matrix} C \begin{matrix} \diagup OH \\ \diagdown CH_3 \end{matrix} + Mg(OH)I$$

$$2Mg(OH)I + 2HC_2H_3O_2 = MgI_2 + Mg(C_2H_3O_2)_2 + 2H_2O.$$
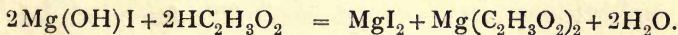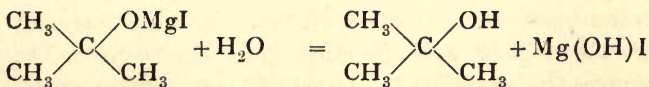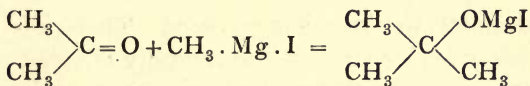
The above example is intended to show the most general method of preparation and use of Grignard's reagents. As will be seen later, under certain circumstances, the method needs to be modified by more careful regulation of temperature and by avoidance of the use of water or acid. For the prepara-

tion of small quantities of the reagent, it is generally sufficient to mix the ether, magnesium, and all the alkyl or aryl halide in a flask provided with a reflux condenser.

EXPERIMENTAL DETAILS.

The following points are of general interest:—

It is essential that all apparatus and materials employed should be thoroughly dry, and that all access of moisture and carbon dioxide to the reacting mixture should be avoided. This may be sufficiently assured by providing the upper end of the condenser with a tube, one half of which is filled with calcium chloride, the other half with soda-lime. It should be further noted that the reagent is not entirely insensitive to the action of oxygen of the air. For this reason, some chemists prefer to exclude the latter by the passage of a slow current of dry hydrogen through the reaction mixture. This precaution, however, is by no means universally adopted.

Magnesium may be conveniently employed either in the form of turnings or ribbon. The latter should be thoroughly rubbed with fine emery-paper to remove the superficial coating of oxide, wiped clean, and cut into lengths of 1-2 cms. The filings should be cleansed from grease by treatment with alcohol and ether, and dried by heating in the steam-oven.

The following method of purifying and drying commercial ether has been found to yield satisfactory results. The ether (500-1000 c.c.) is shaken with three successive portions (each about 100 c.c.) of dilute sulphuric acid, washed with water, and dried

over plenty of calcium chloride during two or three days, after which it is filtered, allowed to stand in contact with sodium wire until evolution of hydrogen ceases, and then distilled. The distillate is preserved over a small quantity of sodium wire in a bottle provided with a chloride of calcium tube. Immediately previous to use it may be distilled over phosphorus pentoxide, but this latter precaution is not always necessary. Dryness of the ether is essential to success. The presence of the minutest trace of water betrays itself by the formation of a white cloudiness at the commencement of a Grignard's reaction.

The alkyl (aryl) halide used should be carefully dried.

Use of Catalyst to Expedite the Formation of Grignard's Reagents.—It is generally found that aliphatic bromides and iodides attack magnesium with great readiness, whereas aryl bromides and iodides as well as aliphatic chlorides of complex structure sometimes react with difficulty or not at all. In the latter case, addition of a trace of iodine or of methyl iodide is frequently sufficient to start the reaction, which then proceeds without difficulty. The influence of iodine in the case of chlorides is attributed by Wohl[3] to the formation of magnesium iodide, which then converts the chlorides into the more reactive iodides according to the following scheme :—

$$Mg + I_2 \qquad\qquad = \quad MgI_2$$
$$2RCl + MgI_2 \qquad = \quad 2RI + MgCl_2$$
$$2RI + 2Mg \qquad\quad = \quad 2R \cdot MgI$$
$$2R \cdot MgI + 2R \cdot Cl \;=\; 2R \cdot MgCl + 2RI.$$
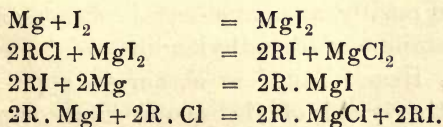
On the other hand, Baeyer and Villiger[4] found that no reaction took place when an ethereal solution of bromo- or iodoaniline or -dimethylaniline was boiled for days with magnesium, with or without addition of iodine. Sachs and Ehrlich[5] confirmed this result, but brought p-bromodimethylaniline into reaction with magnesium in the following manner: The magnesium was acted on by an ethereal solution of ethyl bromide; the bulk of the latter was poured off and replaced by an ethereal solution of p-bromo-dimethylaniline, when the magnesium was attacked by the latter. Baeyer[6] raised the objection that the reaction was not quantitative and the reagent was contaminated with magnesium ethyl bromide. To avoid this, he proposed to "activate" the magnesium by covering it with a thin film of magnesium iodide, which could be effected by heating magnesium in portions of about 10 grams, with continuous shaking, over a free flame and adding half its weight of iodine in small portions, and in such a manner that a new portion was not added until the whole of the previous portion had been consumed. The temperature must be high, but not sufficient to cause the mass to melt. With the given quantity of magnesium, the operation could be completed in a quarter to half an hour. The "activated" magnesium so obtained was a dull grey powder which became brown in course of time and required to be carefully protected from moisture. It reacted readily with an ethereal solution of o-, m-, or p-iodoaniline or -dimethylaniline.

Again, Hesse[7] failed to obtain an approximately quantitative yield of the magnesium compound of

pinene hydrochloride when iodine, aluminium chloride, alkyl halides, etc., were used as catalysers. The method of Ehrlich and Sachs (see above) gave, at first, no better results, but when modified in such a manner that the solution of pinene hydrochloride was added to the magnesium whilst it was reacting vigorously with a readily attackable alkyl halide, led to the formation of an 80-85 per cent. yield of the desired magnesium compound. Hesse concludes that, in the reaction studied by him, the magnesium alkyl halides and not the alkyl halides themselves are the actual catalysers.[8]

It has occasionally been observed that the ether may contain substances which retard the formation of Grignard's reagent, i.e. negative catalysers. Bischoff[9] found that the interaction of magnesium powder and ethylene dibromide in ethereal solution was retarded by the presence of phenetol or ethyl acetate, or of small quantities of acetone, acetophenone, benzophenone, ethyl oxalate, ethyl malonate, or ethyl succinate, even in the presence of iodine. Larger quantities of the latter six substances prevented reaction. Ahrens and Stapler[10] found that the method of desiccation of the ether exerted considerable influence on the course of the interaction of the same two substances. This is in accord with the observation of Freundler and Damond,[11] that the violence of the interaction of trioxymethylene and magnesium sec. butyl bromide in ethereal suspension can be diminished by the addition of a few drops of carbon disulphide.

Use of Solvents other than Ether.—Although

ether is by far the commonest solvent employed in the preparation of Grignard's reagents, its use is by no means essential. Spencer and Stokes [12] found that when certain aryl halides, such as iodobenzene, p-iodotoluene, m-bromoaniline, p-bromophenol, or a-bromonaphthalene, are heated at their boiling-points with magnesium powder, an energetic action occurs, and that the products so obtained, according to their reaction with water, can be represented by the general formula R . MgHal. Similarly, Spencer and Crewdson [13] showed that aryl chlorides and all the lower alkyl halides up to the butyl derivatives only react with magnesium when heated to about 270° in a sealed tube during several hours, whilst alkyl halides higher in the series than the butyl derivatives react with magnesium when they are heated with it at their boiling-points for a few minutes. The reaction is regarded as taking place along the lines indicated by the equations:

$$R . Hal + Mg = R . MgHal.$$
$$2R . Hal + Mg = R - R + MgHal_2.$$
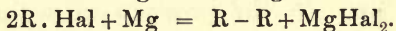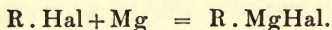
In addition to these compounds, however, unsaturated hydrocarbons are always found in the gaseous portion of the reaction products obtained from all interactions effected in sealed tubes. These unsaturated hydrocarbons, containing both olefines and acetylenes, are probably due to the action of heat on the original halides or on the initial products of the reaction. [14] Similar experiments are recorded by Spencer. [15]

Tschelinzew, [16] in agreement with previous observa-

tions of Bruhl[17] and Malmgren,[18] showed quite generally that magnesium alkyl salts can be obtained by heating magnesium with alkyl halides to a sufficiently high temperature in the presence of a variety of solvents, notably of xylene. In these cases, however, the reaction between the metal and alkyl halide is greatly facilitated by the addition of a trace of diethyl ether, anisole, or of a tertiary amine such as dimethylaniline, which appears to play the part of catalyser. Tschelinzew, indeed, proposed to prepare Grignard's reagents by the interaction of magnesium and alkyl halide in benzene solution in the presence of a trace of dimethylaniline, addition of a minute quantity of iodine being often useful in starting the reaction. In the hands of other investigators, however, the method has not led to satisfactory results.[19] The so-called "individual" magnesium alkyl salts thus obtained (so named because, unlike the Grignard's reagents prepared in ethereal solution, they do not contain combined solvent) form loose, white masses, readily soluble in ether or in a mixture of ether and benzene. They decompose at a high temperature without melting. Their isolation is, in general, quite unnecessary when they are to be used for synthetic purposes, since reaction can generally be brought about in ethereal or hydrocarbon solution. This may be regarded, indeed, as one of the great advantages of Grignard's reagents.

The Quantitative Formation of Grignard's Reagents. — It need scarcely be pointed out that calculated quantities of alkyl (aryl) halide and magnesium should be employed, and that the reaction

should be brought as nearly as possible to completion. Solution of all the magnesium can rarely be secured if the calculated quantity of halide is employed, but, in most cases, the quantity of residual metal should be very small.

Replacement of Magnesium by other Metals.— Beckmann[20] has shown that finely divided calcium reacts with an ethereal solution of iodobenzene or ethyl iodide, with the formation of compounds of the formula

$$C_2H_5 \diagdown \diagup R$$
$$ O$$
$$C_2H_5 \diagup \diagdown CaI$$
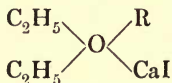
which resemble the Grignard reagents, whilst Spencer and Wallace[21] observe that aluminium, thallium, indium, and lithium form complexes, when heated with alkyl or aryl halides, which yield hydrocarbons when treated with water. These complexes are not formed, however, in the presence of ether. Zeltner[22] finds that the capacity of metals to form organo-metallic derivatives, which commences with the metals of the first group of the Periodic System, reaches its maximum in the metals of the second group, and diminishes in the metals of Groups III., IV., and V. The elements of Groups VI. and VII. show no tendency to form organometallic compounds, but this tendency reappears in the transition Group VIII. The stability of organometallic compounds of metals of the same group increases with the atomic weight of the metal and the size of the organic radical.

Mode of Employment of Grignard's Reagents.— The usual procedure in employing Grignard's reagents

is that already exemplified in the preparation of trimethylcarbinol, and divides itself into two parts: (1) preparation of the reagent; (2) use of the reagent so prepared. Davies and Kipping [23] point out that this method is not invariably necessary, that it generally involves the use of considerable volumes of solvent, and, frequently, waste of the halogen compound employed on account of the formation of by-products. The method originally employed by Barbier [24]—in which the organomagnesium compound is not separately prepared—frequently gives excellent results, and is, in certain cases, preferable to that usually adopted. Thus, · Jaworsky [25] has prepared unsaturated alcohols by treating ketones with magnesium and allyl bromide or iodide in the presence of ether, although magnesium allyl halides of the usual type are unknown. Analogous observations have been made by Oddo,[26] who finds that similar reactions can be carried out in the presence of an inert solvent such as benzene which has been freed from all traces of ether or tertiary base, and under conditions in which magnesium exerts no action on the alkyl iodide alone. Thus, in the presence of benzene, dimethylethylcarbinol is obtained from acetone, ethyl iodide, and magnesium.

Scope of the Reaction.—In the following section, various syntheses effected by means of the Grignard reagents will be treated. In the allotted space, it is impossible to enumerate all the compounds prepared by means of these reagents, but it is hoped to deal with the more important classes of syntheses which have been accomplished by their aid. The

behaviour of magnesium alkyl compounds will be seen, in general, to strongly resemble that of the zinc alkyls. Over these latter compounds the former possess the great advantages that they are more readily prepared, are not spontaneously inflammable, do not usually require to be isolated in the pure state, and have greater reactivity, doubtless due to the more electropositive character of the metal.

SECTION II.

## The Products formed by the Aid of Grignard's Reagents.

Saturated Hydrocarbons.

WHEN water is added to a Grignard's reagent, an energetic action ensues whereby a saturated hydrocarbon is formed:

$$CH_3 . MgI + H_2O = CH_4 + Mg(OH)I.$$

Dilute acids,[27] ammonia or amines,[28] bring about the same result:

$$C_2H_5 . MgI + NH_3 = C_2H_6 + Mg(NH_2)I,$$

as do also alcohols, and, in general, substances which contain the hydroxyl group:

$$CH_3MgI + C_2H_5OH = CH_4 + Mg(OC_2H_5)I.$$
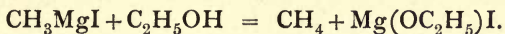
From many points of view, the most convenient agent for bringing about this change is dry powdered ammonium chloride:[29]

$$2CH_3MgI + NH_4Cl = 2CH_4 + NH_2MgI + MgICl.$$
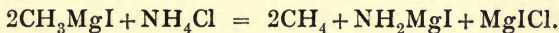
The evolution of methane, which occurs when magnesium methyl iodide is mixed with a substance containing the hydroxyl group, has been employed for the detection and estimation of the latter in organic substances.[30] For this purpose, Zerewitinoff prepares a solution of magnesium methyl iodide in dry amyl ether to which pyridine is added, since amyl ether has insufficient solvent action upon many substances containing the hydroxyl group. A known

13

weight of the substance under examination is treated with an excess of the reagent and the volume of methane evolved is measured. Reaction must be carried out at the ordinary temperature and with all reasonable speed, since pyridine on long standing, more quickly on heating, reacts with evolution of a gas.

The same reaction has been applied [31] to the estimation of active hydrogen generally in organic compounds, *i.e.*, to hydrogen contained in the sulphydryl, imido-, and amido-groups, and in certain tantomeric substances, and also [32] to the estimation of small quantities of water in substances such as coal, starch, etc.

It is worthy of notice that allelotropic substances frequently behave towards Grignard's reagents as if they were entirely hydroxylic in structure. McKenzie [33] has shown that menthyl acetoacetate reacts according to the formula, $CH_3 . C (OH) : CH . COOC_{10}H_{19}$, and not as $CH_3 . CO . CH_2 . COOC_{10}H_{19}$.

In the formation of Grignard's reagents a second reaction—analogous to the Würtz synthesis of hydrocarbons from sodium and alkyl halides—occurs, by which hydrocarbons, formed by the union of the two alkyl radicles of the alkyl halide, are produced :

$$C_2H_5I + Mg + I . C_2H_5 = MgI_2 + C_2H_5 . C_2H_5.$$
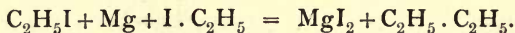
This "synthetic" action only takes place to a small extent in the case of halides of the lower members of the paraffin series. The quantity of by-product increases with increasing molecular weight of the halide until, with the hexyl iodides, it has become

the main product of the reaction. Similarly, diphenyl is invariably formed when magnesium acts upon phenyl bromide or iodide :

$$2C_6H_5Hal + Mg = C_6H_5 . C_6H_5 + MgHal_2.$$
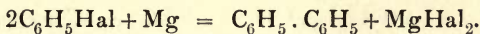
This "synthetic" action of the magnesium may sometimes be considerably eliminated by careful regulation of the temperature during the formation of the reagent.[34]
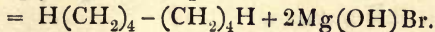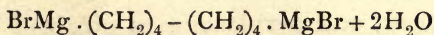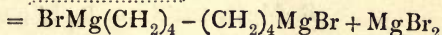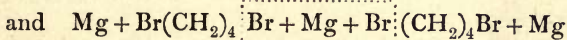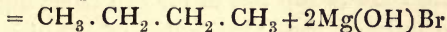
An interesting study of the action of magnesium on dihalogen compounds has been made by v. Braun and Sobecki.[35] Inspection shows that from a normal dihalogen compound of the type $Br(CH_2)_nBr$, a variety of products might be expected; for, on the one hand, if the metal acts merely by the removal of halogen, polymethylenes of the structure

$$\overline{|-(CH_2)_n|} \quad or \quad \overline{|-(CH_2)_n - (CH_2)_n|}$$
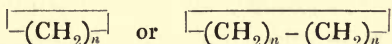
might occur in the final product, whilst, on the other hand, open chain derivatives, such as

$$BrMg(CH_2)_nMgBr, \quad or \quad BrMg(CH_2)_n - (CH_2)_nMgBr,$$

might result. With $\alpha\delta$-dibromobutane and the higher members of the series, substances of the latter two types are produced, thus :

$$Br(CH_2)_4Br + 2Mg = BrMg(CH_2)_4MgBr$$

$$BrMg . (CH_2)_4MgBr + 2H_2O$$
$$= CH_3 . CH_2 . CH_2 . CH_3 + 2Mg(OH)Br$$

and $Mg + Br(CH_2)_4 \overline{Br + Mg + Br}(CH_2)_4Br + Mg$
$$= BrMg(CH_2)_4 - (CH_2)_4MgBr + MgBr_2$$

$$BrMg . (CH_2)_4 - (CH_2)_4 . MgBr + 2H_2O$$
$$= H(CH_2)_4 - (CH_2)_4H + 2Mg(OH)Br.$$
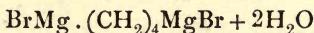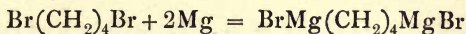
$a\epsilon$-Dibromopentane yielded pentane, n-decane, penta-decane, $CH_3(CH_2)_{13}CH_3$, and higher homologues; $a\eta$-dibromoheptane yielded n-heptane and tetra-decane, $CH_3 . (CH_2)_{12} . CH_3$, whilst $a\kappa$-di-iododecane yielded decane, eicosane, $CH_3(CH_2)_{18}CH_3$, and tetra-contane, $CH_3(CH_2)_{38}CH_3$. Tissier and Grignard,[36] on the other hand, have shown that ethylene is the sole product of the action of ethylene dibromide, and magnesium, whilst Zelinsky and Gutt[37] found that $a\gamma$-dibromopropane and magnesium yielded almost entirely a mixture of trimethylene and propylene with only minute quantities of the magnesium compound of hexamethylene dibromide, $BrMg . (CH_2)_6 . MgBr$.

Gomberg and Cone[38] have succeeded in replacing the chlorine atom in triphenylmethyl chloride by a variety of alkyl groups, by the action of a solution of the former in benzene upon an ethereal solution of the organomagnesium salt. Reaction occurs in accordance with the equation:

$$(C_6H_5)_3C . Cl + R . MgCl = (C_6H_5)_3C . R + MgCl_2.$$
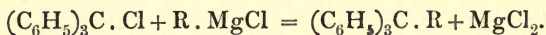
Similarly, Werner and Zilkens[39] have obtained hydrocarbons by the interaction of methyl sulphate and magnesium alkyl halides:

$$(CH_3)_2SO_4 + R . MgCl = R . CH_3 + CH_3(MgCl)SO_4.$$
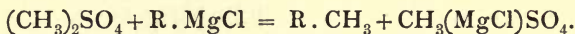
And Houben[40] has in certain cases obtained analogous results by the substitution of alkyl halide for methyl sulphate:

$$R . MgBr + R'Br = R . R' + MgBr_2.$$
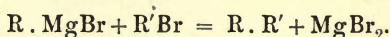
Ethyl benzene, toluene, and p-xylene were obtained in this manner.

Unsaturated Hydrocarbons.

Reference to the production of ethylene and propylene from ethylene dibromide and $\alpha\gamma$-dibromopropane respectively has already been made (see above).

Alcohols are the normal products of the interaction of Grignard's reagents with aldehydes and ketones. Many of these readily pass by loss of water into unsaturated hydrocarbons, whilst some are so unstable that they cannot themselves be isolated. Thus, by the action of magnesium benzyl bromide upon benz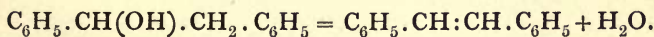aldehyde, Hell[41] obtained phenylbenzylcarbinol, which, when distilled, eliminated water with the formation of stilbene :

$$Mg + C_6H_5CH_2 . Br = C_6H_5CH_2 . MgBr$$

$$C_6H_5 . C\underset{O}{\overset{H}{<}} + C_2H_5CH_2 . MgBr = C_6H_5 . C\underset{CH_2 . C_6H_5}{\overset{H}{\underset{}{-}}} O . MgBr$$

$$C_6H_5 . C\underset{CH_2 . C_6H_5}{\overset{H}{-}}OMgBr + H_2O = C_6H_5 . C\underset{CH_2 . C_6H_5}{\overset{H}{-}}OH + Mg(OH)Br$$

$$C_6H_5 . CH(OH) . CH_2 . C_6H_5 = C_6H_5 . CH:CH . C_6H_5 + H_2O.$$
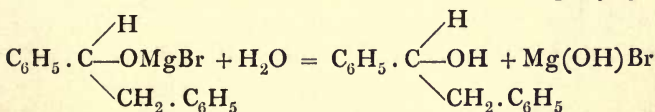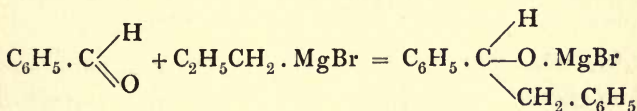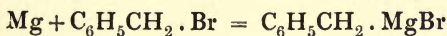
Whilst magnesium benzyl chloride and anisaldehyde yielded p-methoxystilbene, $CH_3O . C_6H_4 . CH:CH . C_6H_5$, as immediate product. Similarly, Hell and Stockmayer obtained anisylphenylpropene,

$$\underset{CH_3O . C_6H_4}{\overset{C_6H_5}{>}}C:CH . CH_3,$$

B
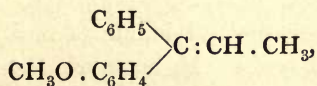
as immediate product of the action of magnesium ethyl iodide upon anisylphenylketone. Analogous results are recorded by Hell and Wiegandt [42] and by F. and L. Sachs. [43]

A similar interesting application of this reaction is found in the formation of $\Delta^{3\cdot8(9)}$-p-menthadiene, which was obtained by Kay and Perkin [44] by the action of excess of magnesium methyl iodide on optically active ethyl-Δ^3-tetrahydro-p-toluate,

$$CH_3 . CH \underset{CH_2-CH_2}{\overset{CH_2-CH}{\diagdown}} \diagup C . COOC_2H_5.$$
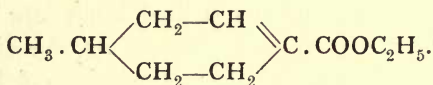
As intermediate compound, Δ^3-p-menthenol, was formed,

$$CH_3 . CH \underset{CH_2-CH_2}{\overset{CH_2-CH}{\diagdown}} \diagup C . C \underset{OH}{\overset{CH_3}{\diagup}} CH_3$$
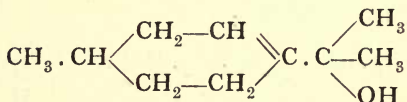
which, when left in contact with an ethereal solution of magnesium methyl iodide at the ordinary temperature, lost water, yielding the optically active, unsaturated hydrocarbon, $\Delta^{3\cdot8(9)}$-p-menthadiene,

$$CH_3 . CH . \underset{CH_2-CH_2}{\overset{CH_2-CH}{\diagdown}} \diagup C . C \underset{CH_2}{\overset{CH_3}{\diagup}}$$
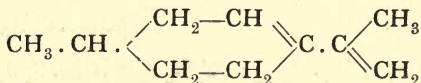
In certain cases it has been found possible to control similar reactions in such a manner that either alcohols or unsaturated hydrocarbons may be produced at will. Grignard [45] showed that phenyl-dimethylcarbinol, $C_6H_5 . C(OH)(CH_3)_2$, is produced when magnesium methyl iodide (1 mol.) reacts with acetophenone (1 mol.). If, however, the reagents are

taken in the proportion of 2 molecules of the former to one of the latter, the ether distilled off after completion of the initial reaction, and the residue then heated at 100° during several hours, metho-(1')-vinyl benzene,

$$\begin{array}{c} C_6H_5 \\ \diagdown \\ \diagup C:CH_2, \\ CH_3 \end{array}$$
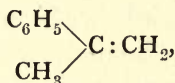
is obtained.

Tiffeneau [46] has succeeded in preparing allyl benzene by the action of magnesium phenyl bromide on allyl bromide,

$$C_6H_5MgBr + BrCH_2 . CH : CH_2$$
$$= C_6H_5 . CH_2 . CH : CH_2 + MgBr_2,$$
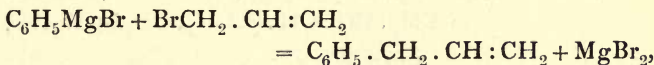
whilst, according to Resseguier [47] allyl*cyclo*hexane results from the action of magnesium *cyclo*hexyl bromide on allyl iodide. The general applicability of the reaction has been demonstrated by v. Braun, Deutsch, and Schmatloch,[48] who have obtained unde-cylene, $C_9H_{19} . CH : CH_2$, from octyl bromide; unde-cadiene, $CH_2 : CH . (CH_2)_7 . CH : CH_2$, from $a\epsilon$-di-iodo-pentane; decadiene, $CH_2 : CH . (CH_2)_6 . CH : CH_2$, from $a\delta$-di-iodobutane; phenylamylene,
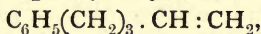
$$C_6H_5(CH_2)_3 . CH : CH_2,$$

from phenylethyl bromide; phenylhexylene,
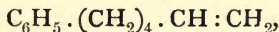
$$C_6H_5 . (CH_2)_4 . CH : CH_2,$$

from phenylpropyl bromide; and phenyloctylene, $C_6H_5 . (CH_2)_6 . CH : CH_2$, from phenylamyl bromide.

According to Oddo,[49] the interaction of magnesium acetylene bromide and water gives acetylene in small yield :

$$HC : CMgBr + H_2O = HC : CH + Mg(OH)Br.$$
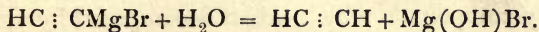
Iodo Compounds.

v. Braun and Deutsch [50] have succeeded in replacing bromine by iodine by the action of free iodine upon the magnesium alkyl bromide. Thus, $\alpha\delta\epsilon$-tribromo-hexane, when treated with magnesium, yielded magnesium hexene bromide, which reacted with iodine with the formation of α-iodo-Δ^δ-hexene:

$$CH_3 . CHBr . CHBr . (CH_2)_2 . CH_2Br + 2Mg$$
$$= CH_3 . CH : CH . (CH_2)_2 . CH_2MgBr + MgBr_2$$

$$CH_3 . CH : CH . (CH_2)_2 . CH_2 . MgBr + I_2$$
$$= CH_3 . CH : CH . (CH_2)_2 . CH_2I + MgIBr.$$
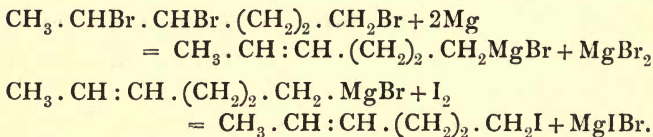
Simultaneously, addition of iodine at the double bond occurred to some extent. In a later paper, v. Braun, Deutsch, and Schmatloch [51] find that this drawback can be avoided if free iodine be replaced by iodoacetonitrile, $I . CH_2CN$, which reacts in accordance with the equation:

$$BrMg . R + I . CH_2CN = RI + Br . Mg . CH_2CN.$$

In this manner, bromobenzene was converted into iodobenzene, phenylpropyl bromide, $C_6H_5(CH_2)_3Br$, into phenylpropyl iodide, and $\alpha\zeta\eta$-tribomoheptane, $BrCH_2 . (CH_2)_4 . CH Br . CH_2Br$, into heptylene iodide, $C_7H_{13}I$.

Alcohols.

Primary Alcohols.—Grignard's reagents have not found a very extensive application in the preparation of primary alcohols. They are capable, however, of absorbing dry oxygen with the formation of oxy-compounds which, when decomposed by water,

yield primary alcohols. Thus, benzyl alcohol may be obtained from benzyl chloride : [52]

$$C_6H_5 . CH_2Cl + Mg = C_6H_5 . CH_2MgCl$$

$$C_6H_5CH_2 . MgCl + O = C_6H_5 . CH_2 . O . MgCl$$

$$C_6H_5CH_2 . O . MgCl + H_2O = C_6H_5 . CH_2OH + Mg(OH)Cl.$$
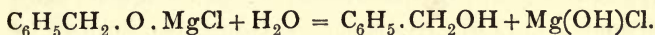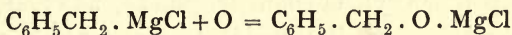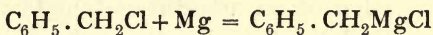
Primary alcohols may also be obtained from the alkyl halides of the next lower series, *i.e.* the halogen atom may be replaced by the group CH_2OH, by the aid of formaldehyde or of its polymer oxymethylene.[53] For this purpose, an ethereal solution of the magnesium alkyl halide is boiled during 1-2 days with oxymethylene. Subsequently a portion of the ether is driven off, the residue heated to a somewhat higher temperature, and finally decomposed by dilute acid :

$$\underset{O}{\overset{H}{C}}{\overset{H}{<}} + C_2H_5 . MgBr = H . C{\overset{H}{<}}{\overset{OMgBr}{C_2H_5}}$$

$$H . C{\overset{H}{<}}{\overset{OMgBr}{C_2H_5}} + H_2O = C_2H_5 . CH_2OH + Mg(OH)Br$$
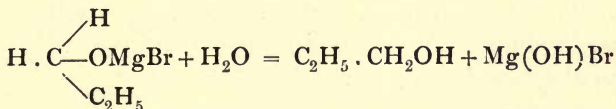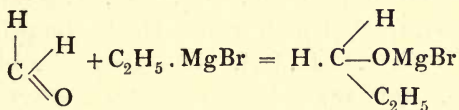
The same method has been employed in rather more complicated cases by v. Braun, Deutsch, and Schmatloch,[54] who obtained, for example, the monophenyl ether of $\alpha\zeta$-hexamethylene glycol,

$$C_6H_5O . (CH_2)_6OH,$$
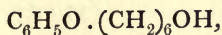
from trioxymethylene and magnesium ε-phenoxyamyl iodide. This result is the more noteworthy since

Grignard[55] found that bromophenetol does not yield
a magnesium derivative, but loses hydrobromic acid
with the formation of an unsaturated hydrocarbon.
As the polymethylene chain lengthens, however, the
normal reaction of the metal becomes much more
pronounced, and Grignard's reagents are formed in
good yield.

Magnesium alkyl halides react readily with ethy-
lene oxide with the formation of primary alcohols.
According to Grignard,[56] the ethylene oxide first
forms an oxonium compound,

$$\begin{array}{c} CH_2 \\ | \\ CH_2 \end{array} \!\!\! > \!\! O \!\! < \!\!\! \begin{array}{c} R \\ \\ MgHal, \end{array}$$
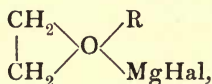
which, after removal of the solvent, becomes trans-
formed into the isomer, $R \cdot CH_2 \cdot CH_2 \cdot O \cdot MgHal$.
The latter, when treated with water, yields the prim-
ary alcohol, $R \cdot CH_2 \cdot CH_2 \cdot OH$. If water be added
directly to the primary addition product, ethylene
oxide is re-formed, which combines with the
magnesium halide simultaneously produced to yield
an alkylene-halhydrin:

$$\begin{array}{c} CH_2 \\ | \\ CH_2 \end{array} \!\!\! > \!\! O + MgBr_2 \quad = \quad \begin{array}{c} CH_2Br \\ | \\ CH_2 \cdot O \cdot MgBr \end{array}$$

$$\begin{array}{c} CH_2Br \\ | \\ CH_2 \cdot O \cdot MgBr \end{array} + H_2O \quad = \quad \begin{array}{c} CH_2Br \\ | \\ CH_2OH \end{array} + Mg(OH)Br$$
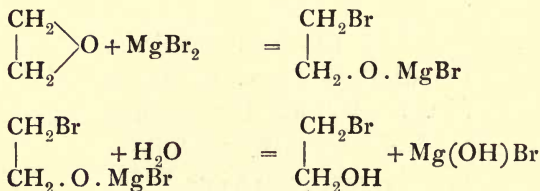
Similar observations are recorded by Blaise.[57]
Henry[58] has extended this method by using propylene

oxide, from which, by the action of magnesium ethyl bromide, he has obtained the secondary alcohol, methyl n-propylcarbinol:

$$CH_3 . CH_2 \underset{\diagdown \diagup}{—} CH_2 + C_2H_5 . MgBr$$
$$O$$

$$= \begin{array}{c} CH_3 . CH . CH_2 . C_2H_5 \\ | \\ O . MgBr \end{array} \longrightarrow \begin{array}{c} CH_3 . CH . CH_2 . C_2H_5 \\ | \\ OH \end{array}$$
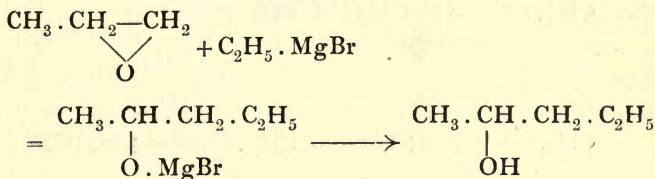
When epichlorhydrin is allowed to react with cold solutions of magnesium alkyl halides, only the hydrogen of the hydroxyl group is replaced by the radical, MgHal. If reaction takes places in warm solution, however, the chlorine atom is also replaced (by alkyl), and decomposition of the reaction-product by ice leads to the formation of primary alcohols: [59]

$$\begin{array}{c} CH_2Cl \\ | \\ CH_2OH \end{array} + R . MgHal = \begin{array}{c} CH_2Cl \\ | \\ CH_2O . MgHal \end{array} + R . H$$

$$\begin{array}{c} CH_2Cl \\ | \\ CH_2O . MgHal \end{array} + R . MgHal = \begin{array}{c} CH_2R \\ | \\ CH_2 . O . MgHal \end{array} + MgCl(Hal)$$

$$\begin{array}{c} CH_2R \\ | \\ CH_2 . O . MgHal \end{array} + H_2O = \begin{array}{c} CH_2 . R \\ | \\ CH_2OH \end{array} + Mg(OH)Hal.$$
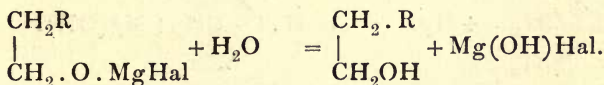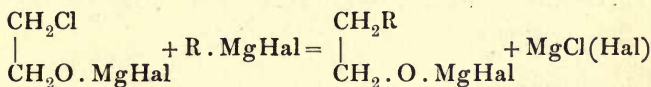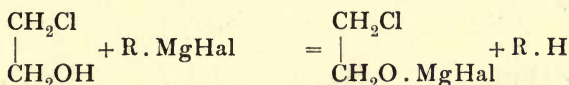
Secondary Alcohols.—These have been obtained in large number, and generally in good yield, by the interaction of Grignard's reagents with aldehydes, other than formaldehyde,[60] and with esters of formic

acid.[61] Thus, acetaldehyde and magnesium methyl iodide yielded *iso*propyl alcohol,

$$CH_3 . C{\overset{H}{\underset{O}{}}} + CH_3MgI = CH_3 . C{\overset{H}{\underset{CH_3}{}}}{-}OMgI$$

$$CH_3 . C{\overset{H}{\underset{CH_3}{}}}{-}OMgI + H_2O = CH_3 . C{\overset{H}{\underset{CH_3}{}}}{-}OH + Mg(OH)I$$
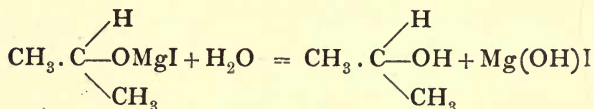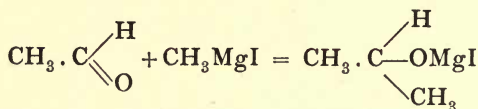
Similarly, benzaldehyde and magnesium methyl iodide yielded phenylmethylcarbinol, $C_6H_5 . CHOH . CH_3$.

*Iso*propyl alcohol was also obtained from ethyl formate and magnesium methyl iodide in accordance with the equations:

$$H . C{\overset{O}{\underset{OC_2H_5}{}}} + CH_3MgI = H . C{\overset{OMgI}{\underset{OC_2H_5}{}}}{-}CH_3$$

$$H . C{\overset{OMgI}{\underset{OC_2H_5}{}}}{-}CH_3 + CH_3 . MgI = H . C{\overset{OMgI}{\underset{CH_3}{}}}{-}CH_3 + Mg(OC_2H_5)I$$

$$H . C{\overset{OMgI}{\underset{CH_3}{}}}{-}CH_3 + H_2O = H . C{\overset{OH}{\underset{CH_3}{}}}{-}CH_3 + Mg(OH)I$$
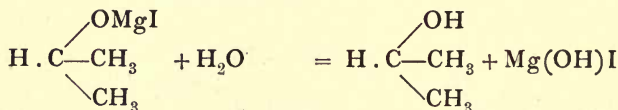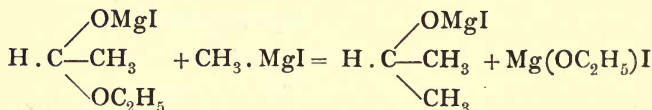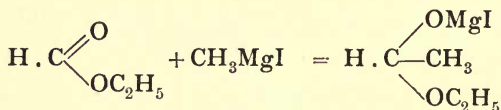
Tertiary Alcohols.—These may be readily obtained by the action of Grignard's reagents on ketones, esters other than those of formic acid, acid chlorides, and anhydrides. Thus, triphenylcarbinol may be obtained by the action of magnesium phenyl bromide

on benzophenone or ethyl benzoate, according to the schemes:

I.
$$C_6H_5 \diagdown C = O + C_6H_5 . MgBr = \quad C_6H_5 \diagdown C \diagup OMgBr$$
$$C_6H_5 \diagup \qquad\qquad\qquad C_6H_5 \diagup \diagdown C_6H_5$$

$$C_6H_5 \diagdown C \diagup OMgBr \quad + H_2O \quad = \quad C_6H_5 \diagdown C \diagup OH \quad + Mg(OH)Br$$
$$C_6H_5 \diagup \diagdown C_6H_5 \qquad\qquad\qquad C_6H_5 \diagup \diagdown C_6H_5$$

II.
$$C_6H_5 . C \diagup O \diagdown OC_2H_5 + C_6H_5MgBr = C_6H_5 . C \diagup OMgBr \diagdown C_6H_5 \diagdown OC_2H_5$$

$$C_6H_5 . C \diagup OMgBr \diagup C_6H_5 + C_6H_5MgBr = C_6H_5 . C . C_6H_5 + Mg \diagup OC_2H_5 \diagdown Br$$
$$\diagdown OC_2H_5 \qquad\qquad\qquad \diagdown C_6H_5$$

$$C_6H_5 . C \diagup OMgBr \diagup C_6H_5 + H_2O = C_6H_5 . C \diagup OH \diagup C_6H_5 + Mg \diagup OH \diagdown Br$$
$$\diagdown C_6H_5 \qquad\qquad\qquad \diagdown C_6H_5$$
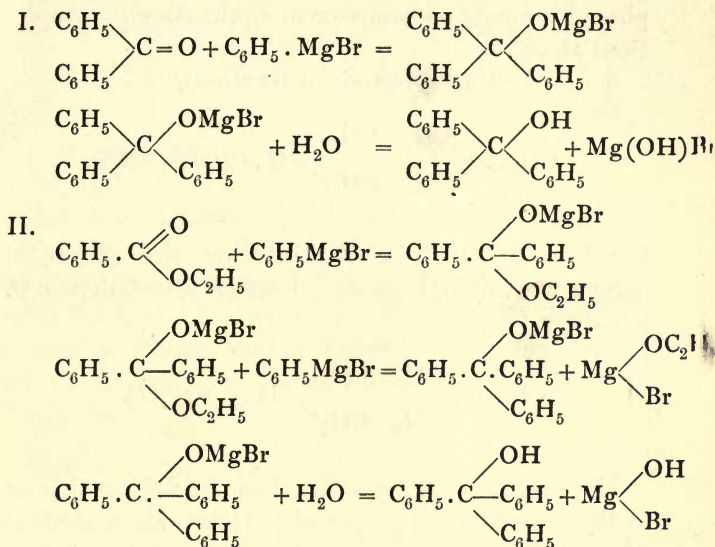
Tertiary alcohols may likewise be obtained from cyclic ketones: thus, Murat [62] transformed *l*-menthone (Formula I.) into *l*-3-phenyl-1-methyl-4-*iso*propyl-3-*cyclo*hexanol (Formula II.),
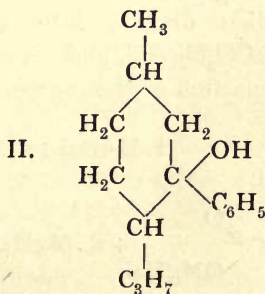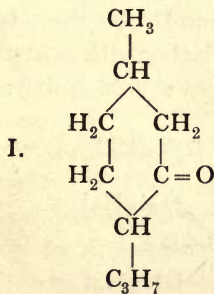
Similarly, Jermain and Creighton[63] obtained phenyl-borneol, $C_{10}H_{16} . C_6H_5 . OH$, by the action of magnesium phenyl bromide on camphor in equimolecular proportions at 60°.

An interesting synthesis of terpineol,

$$CH_3 . C \underset{CH_2-CH_2}{\overset{CH-CH_2}{\diagup\diagdown}} CH . C(OH)(CH_3)_2,$$
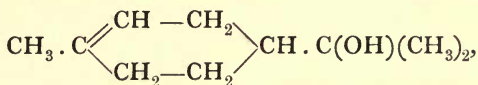
has been effected by Perkin[64] by the action of magnesium methyl iodide on ethyl Δ^3-tetrahydro-p-toluate,

$$CH_3 . C \underset{CH_2-CH_2}{\overset{CH-CH_2}{\diagup\diagdown}} CH . COOC_2H_5.$$
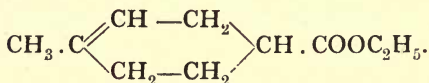
The reactions employed are thus precisely analogous to those used in the preparation of secondary alcohols from aldehydes or formic esters. A modification of the second reaction, in which all three alkyl radicals of the tertiary alcohol are supplied in the form of their organomagnesium compounds, consists in converting the compound AlkMgHal by means of dry carbon dioxide into a compound of the type $AlkCO_2MgHal$, and treating the latter with a further proportion of the organomagnesium salt (2 mols.):[65]

$$R . MgHal + CO_2 = R . CO_2MgHal$$

$$R . C \overset{O}{\underset{OMgHal}{\diagup\diagdown}} + R . MgHal = R . C \overset{OMgHal}{\underset{OMgHal}{\diagdown\diagup}} R$$

$$R \cdot C \overset{O \cdot MgHal}{\underset{O \cdot MgHal}{\diagdown}} R \quad + R \cdot MgHal = R \cdot C \overset{R}{\underset{OMgHal}{\diagdown}} R + MgO + MgHal_2$$

$$R \cdot C \overset{R}{\underset{OMgHal}{\diagdown}} R \quad + H_2O \quad = R \cdot C \overset{R}{\underset{OH}{\diagdown}} R \cdot + Mg(OH)Hal.$$
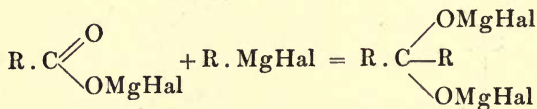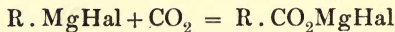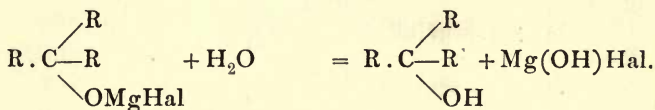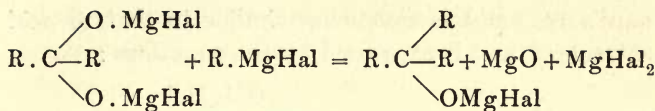
Another method of obtaining tertiary alcohols, which is very similar to that given above, consists in allowing an excess of Grignard's reagent to react with the free acid (see also p. 42).

Acid chlorides behave towards magnesium alkyl salts in a manner similar to esters: [66]

$$R \cdot C \overset{O}{\underset{Cl}{\diagdown}} + 2R'MgHal = R \cdot C \overset{OMgHal}{\underset{R'}{\diagdown}} R' + MgClHal$$

$$R'_2 \cdot R \cdot C \cdot OMgHal + H_2O = R'_2 \cdot R \cdot C \cdot OH + Mg(OH)Hal.$$
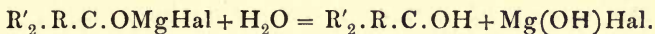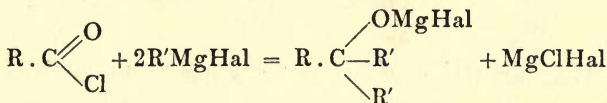
Carbonyl chloride, when treated with organo-magnesium compounds (2 mols.) yields a mixture of secondary and tertiary alcohols which frequently contains unsaturated hydrocarbons. In the methane and ethane series the action of magnesium alkyl halide (3 mols.) on carbonyl chloride (1 mol.) leads exclusively to tertiary alcohols, whereas in the higher series secondary alcohols are simultaneously produced.[67] Tertiary alcohols may also be obtained in small quantity from carbon oxysulphide, COS, and Grignard's reagent.[68]

The behaviour of acid anhydrides towards Grig-

nard's reagents is somewhat similar to that of acid chlorides,[69] and is expressed by the equations:

$$R-C\underset{R-C}{\overset{\diagup O}{\diagdown}}O + R.MgHal = R-C\overset{\diagup OMgHal}{\underset{\diagdown}{-R}}O \atop R-C\diagdown_O^{\diagup O}$$

$$2 \quad R-C\overset{\diagup OMgHal}{\underset{\diagdown}{-R}}O + 2R.MgHal = 2R.\overset{\diagup OMgHal}{\underset{\diagdown}{R}}-R + Mg(O.COR)_2 + MgHal_2$$
$$R-C\diagdown_O$$

$$R.C\overset{\diagup OMgHal}{\underset{\diagdown R}{-R}} + H_2O = R.C\overset{\diagup OH}{\underset{\diagdown R}{-R}} + Mg(OH)Hal.$$
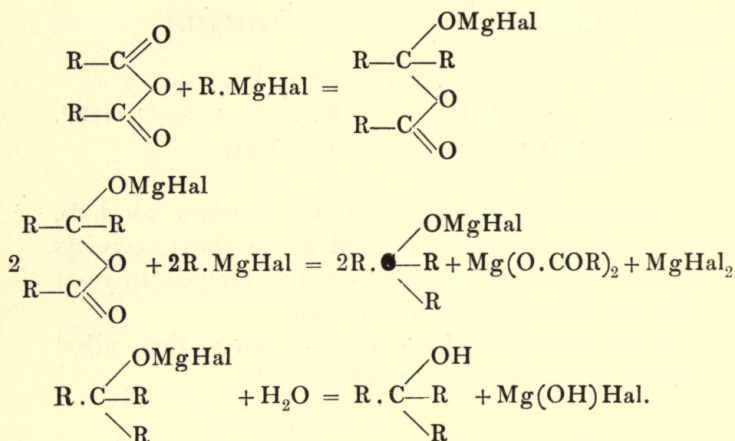
The interaction of acetic anhydride and its homologues with magnesium alkyl halides has been made the subject of further investigation by Fournier,[70] who finds that, under certain circumstances, ketones are produced in addition to tertiary alcohols. The chief reactions which occur are represented by the equations:

$$R.CO \atop R.CO \diagup^{\diagdown} O + R'.MgBr = R.CO \atop R.C-OMgBr \diagup^{\diagdown}_{R'} O$$

$$R.CO \atop R.C-OMgBr \diagup^{\diagdown}_{R'} O + H_2O = Mg(OH)Br + R.CO_2H + R.O.R'$$
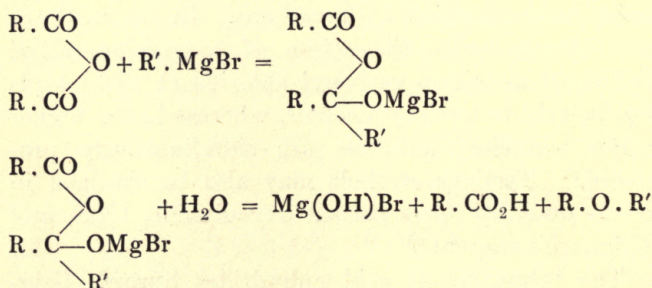
Thus, when magnesium ethyl bromide (1 mol.) was slowly added to an ethereal solution of acetic anhydride (1 mol.), cooled in a mixture of ice and salt, and the mixture decomposed after three hours by ice-cold water, methyl ethyl ketone was obtained.

The investigation of the interaction of succinic anhydride and magnesium organic halides has been carried out by Houben and Hahn,[71] who found that reaction did not readily take place, but ultimately led to the formation of ditertiary glycols of the type $(HO)R_2C.CH_2-CH_2.C(OH)R_2'$. Phthalic anhydride behaved similarly towards magnesium p-tolyl bromide yielding o-di-p-toluoylbenzene, $C_6H_4(CO.C_6H_4.CH_3)_2$, but, when treated with magnesium methyl, ethyl, or propyl halides, it gave dimethyl-, dietheyl-, and dipropylphthalide respectively,[72]
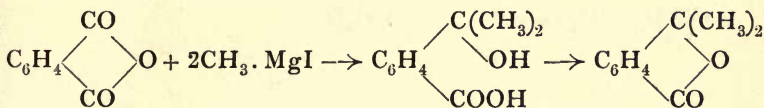
whilst camphoric anhydride and ¡magnesium benzyl chloride yielded the two isomeric campholides,[73]
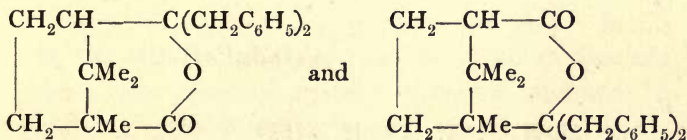
Primary Tertiary α-Glycols.—These may be prepared by the action of magnesium alkyl halides on

glycerine a-chlorhydrin.[74] Thus, magnesium amyl bromide yielded the compound

$$\begin{array}{c} CH_3 \\ \diagdown \\ C_5H_{11} \diagup \end{array} C(OH).CH_2OH,$$
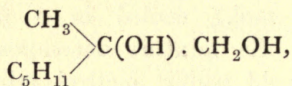
together with small quantities of the glycol,

$$C_5H_{11}.CH_2.CH(OH).CH_2OH.$$
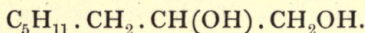
Monoalkyl ethers of primary tertiary glycols have been obtained by Béhal and Sommelet[75] from ethoxy-acetic esters or ethoxyketones:

$$OC_2H_5.CH_2.C\diagup^O_{\diagdown OC_2H_5} \quad +2R.MgHal$$

$$= OC_2H_5.CH_2.C\diagup^{OMgHal}_{\diagdown R}{}-R \quad +Mg(OC_2H_5)Hal$$

$$OC_2H_5.CH_2.C\diagup^{OMgHal}_{\diagdown R}{}-R \quad +H_2O$$

$$= OC_2H_5.CH_2.C\diagup^{OH}_{\diagdown R}{}-R \quad +Mg(OH)Hal$$

$$\begin{array}{c} R \\ \diagdown \\ O \diagup \end{array} C.CH_2.OC_2H_5 +R.MgHal$$

$$= \begin{array}{c} R \\ \diagdown \\ R \diagup \end{array} C(OMgHal).CH_2.OC_2H_5$$

$$\begin{array}{c} R \\ \diagdown \\ R \diagup \end{array} C(OMgHal).CH_2.OC_2H_5 +H_2O$$

$$= \begin{array}{c} R \\ \diagdown \\ R \diagup \end{array} C(OH).CH_2.OC_2H_5 +Mg(OH)Hal.$$

Secondary Tertiary Glycols.—Compounds of the type $R.CHOH.C(OH).R.R$ have been obtained by Acree [76] by the action of Grignard's reagents upon r-benzoin, $C_6H_5.CH(OH).CO.C_6H_5$, and methyl r-mandelate, $C_6H_5.CHOH.COOCH_3$.[77] A similar series of optically active glycols have been prepared by McKenzie and Wren [78] from l-benzoin and methyl l-mandelate.

Ditertiary Glycols.—These compounds may be readily obtained according to Valeur [79] by treatment of esters of dibasic acids with excess of an organomagnesium halide. Thus, ethyl oxalate yielded tetramethylglycol when treated with an excess of magnesium methyl iodide:

$$C_2H_5O \underset{}{\overset{O}{\diagdown}} C\!-\!C \overset{O}{\underset{OC_2H_5}{\diagup}} + 4CH_3MgI$$

$$= \underset{CH_3}{\overset{IMgO}{\diagdown}} CH_3\!-\!C\!-\!C\!-\!CH_3 \underset{CH_3}{\overset{OMgI}{\diagup}} + 2Mg(OC_2H_5)I$$

$$\underset{CH_3}{\overset{IMgO}{\diagdown}} CH_3\!-\!C\!-\!C\!-\!CH_3 \underset{CH_3}{\overset{OMgI}{\diagup}} + 2H_2O$$

$$= (CH_3)_2C.(OH).C(OH)(CH_3)_2 + 2Mg(OH)I$$

Similarly, Valeur [80] and Dilthey and Last [81] found that the final products of the interaction of succinic esters and excess of organomagnesium salts are ditertiary glycols of the type
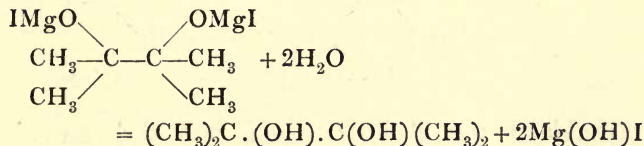
$$\underset{OH}{\overset{R}{\diagdown}} R\!-\!C.CH_2.CH_2.C\!-\!R \underset{OH}{\overset{R}{\diagup}}$$

Ethyl phthalate, on the other hand,[82] appears to yield phthalides in the first place:

$$C_6H_4\left\langle\begin{array}{c}COOR\\COOR\end{array}\right. + 2R'MgHal$$

$$= C_6H_4\left\langle\begin{array}{c}\begin{array}{c}OMgHal\\C-R'\\\backslash R'\end{array}\\COOR\end{array}\right. \longrightarrow C_6H_4\left\langle\begin{array}{c}CR'_2\\CO\end{array}\right\rangle O$$
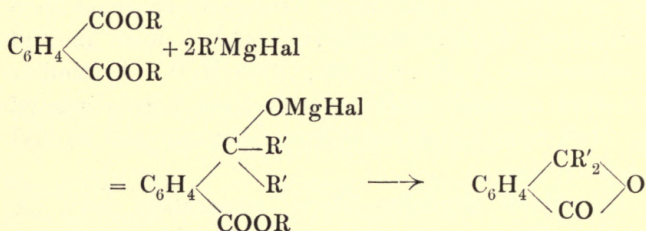
Generally, however, the reaction proceeds a step further, the ketone group contained in the dialkyl-phthalide first formed reacting with another molecule of the Grignard reagent and the resulting compound decomposing on contact with water, with the production of a derivative of phthalan (o-xylylene oxide):

$$C_6H_4\left\langle\begin{array}{c}CR_2^1\\CO\end{array}\right\rangle O + R'MgHal + H_2O$$

$$= C_6H_4\left\langle\begin{array}{c}CR_2^1\\CR'OH\end{array}\right\rangle O \longrightarrow C_6H_4\left\langle\begin{array}{c}CR'_2\\C=R''\end{array}\right\rangle O$$
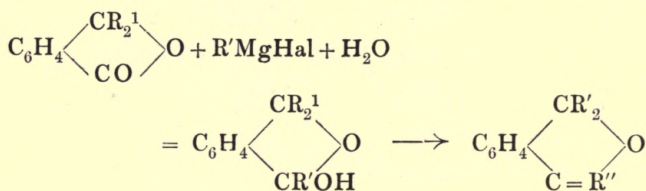
Frankland and Twiss[83] found that the normal action took place when methyl d-tartrate was treated with excess of magnesium phenyl bromide, optically active tetraphenylerithritol,

$$(C_6H_5)_2 . C(OH) . CH(OH) . CH(OH) . C(OH)(C_6H_5)_2,$$
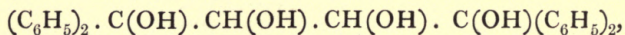
being obtained.

Acree[84] has also obtained ditertiary glycols from a-diketones. Thus, benzil yielded tetraphenyl glycol

when acted on by excess of magnesium phenyl bromide :

$$C_6H_5 . C = O$$
$$\mid \quad + 2C_6H_5MgBr$$
$$C_6H_5 . C = O$$

$$=\quad
\begin{array}{l}
C_6H_5 . C{-}C_6H_5 \\[2pt]
\quad \mid \\[2pt]
C_6H_5 . C
\end{array}
\begin{array}{l}
{}^{OMgBr} \\[10pt]
{}^{OMgBr} \\
{}_{C_6H_5}
\end{array}
\longrightarrow
\begin{array}{l}
C_6H_5 . C{-}C_6H_5 \\[2pt]
\quad \mid \\[2pt]
C_6H_5 . C
\end{array}
\begin{array}{l}
{}^{OH} \\[10pt]
{}^{OH} \\
{}_{C_6H_5}
\end{array}$$

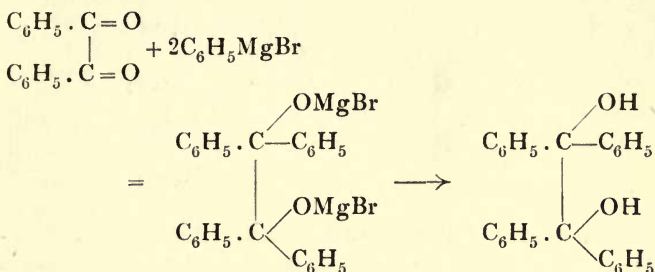It may be pointed out that the benzil molecule contains two carbonyl groups, each of which—as in the case cited above—may be attacked by Grignard's reagent. By a suitable adjustment of the conditions of reaction and the quantities of material employed, Acree was able to limit the action of the reagent to one of the carbonyl groups and thus to obtain, e.g. phenyl benzoin, $C_6H_5 . CO . C(OH)(C_6H_5)_2$.

Bamberger and Blangey[85] have obtained small yields of quinols by the action of Grignard's reagents on p-quinones. The interaction of magnesium ethyl bromide and anthraquinone[86] leads to the production of dihydroxydiethyldihydroanthracene,

$$C_6H_4 {<}^{\text{CEt(OH)}}_{\text{CEt(OH)}} {>} C_6H_4,$$
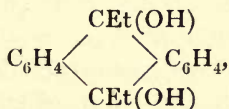
when excess of the Grignard reagent is employed; when, however, anthraquinone is kept in excess, ethyloxanthranol is produced. Werner and Grob[87] have similarly prepared 9 : 10-dihydroxydiphenyldi-

hydrophenanthrene by the action of magnesium phenyl bromide upon phenanthrenequinone :
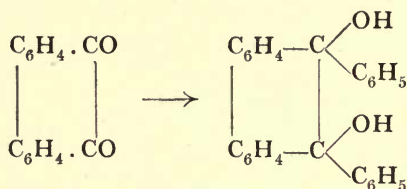
Phenols, Thiophenols, and Selenophenol. — Bodroux[88] found that small quantities of phenols were formed when oxygen was passed through a solution of magnesium aryl halides. This observation is confirmed by Wuyts,[89] who, however, found the action to be rather more complex. Thus, when oxygen was bubbled through an ethereal solution of magnesium phenyl bromide, other phenolic compounds were also formed, together with diphenyl, p-diphenylbenzene, phenylethylcarbinol, and ethyl alcohol. He suggests that, in all probability, a peroxide is the primary compound of the oxidation.

Wuyts[90] found that a thiol was the only product of the action of finely divided sulphur upon organomagnesium compounds, if the reaction was carried out in an atmosphere of dry hydrogen and care was taken to avoid excess of sulphur. The yield attained 80 per cent. of the theoretical. By the action of sulphur on the compound formed by the condensation of the thiol with an additional molecule of the reagent, a disulphide was formed :

$$R \cdot S \cdot H + R \cdot MgHal = R \cdot S \cdot MgHal + R \cdot H$$
$$2R \cdot S \cdot MgHal + S = R-S-S-R + S(MgHal)_2,$$
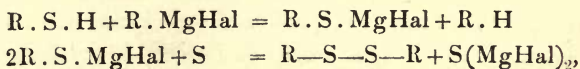
whilst, by the interaction of the disulphide and the organomagnesium salt, a monosulphide was obtained:

$$R—S—S—R + R . MgHal = R—S—R + R—S . MgHal.$$
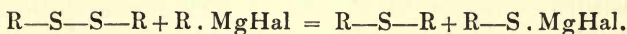
When the same precautions were adopted as in the case of sulphur, selenophenol, C_6H_5SeH, could be obtained by the action of selenium on magnesium phenyl bromide. The yield obtained was 81 per cent. of the theoretical.

Ethers.

Ethers of the type, $R . CH_2 . O . CH_3$, have been prepared by Hamonet[91] by the interaction of Grignard's reagents and halogen substituted methyl ethers. An ethereal solution of chlorodimethyl ether, $ClCH_2 . O . CH_3$, is not attacked by magnesium, and also prevents the solution of the metal by methyl iodide or ethyl bromide. It reacts readily, however, with a solution of magnesium alkyl halide with the production of mixed ethers:

$$CH_3 . O . CH_2Cl + R . MgBr = CH_3 . O . CH_2R + MgBrCl.$$
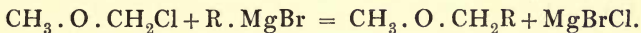
Similar observations have been recorded by Reychler.[92]

Klages[93] has prepared a series of phenol ethers by the action of magnesium alkyl halides on alkoxyalde-hydes; thus, magnesium propyl iodide and anisaldehyde yielded p-butenylanisol:

$$(CH_3O) . C_6H_4 . CH : CH . CH_2 . CH_3.$$
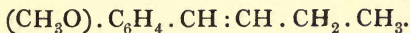
Scission of Phenolic Ethers.—Grignard[94] found that organometallic derivatives do not react with phenolic ethers under ordinary conditions. By adding

magnesium, however, to a mixture of equimolecular proportions of an alkyl bromide with anisole or phenetole, using benzene as solvent, reaction may be brought about. If the resultant product is immediately decomposed, the ether is recovered unchanged; if, however, the solvent is distilled off and the residue heated at 150°-160° under 10-15 mm., only one-half of the ether is recovered, the remainder having undergone conversion into the corresponding phenol. This is explained by supposing that an oxonium complex is first produced by addition and that this undergoes scission, yielding the compound $C_6H_5 . O . MgBr$, together with, probably, ethylene and a saturated hydrocarbon.

Aldehydes.

Aldehydes have been prepared by a number of methods which, generally, involve the action of Grignard's reagents upon derivatives of formic acid. Gattermann and Maffezzoli[95] found that when two molecules of an organomagnesium compound are allowed to react with one molecule of ethyl formate, the main product of the reaction is a secondary alcohol; but if, on the other hand, an excess of the formic ester is employed, an aldehyde is formed according to the following equation:

$$H . C\overset{O}{\underset{OC_2H_5}{\big<}} + IMgR = H . C\overset{R}{\underset{O}{\big<}} + Mg(OC_2H_5)I.$$
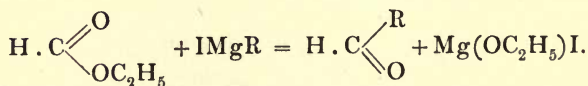
A series of aldehydes has been prepared by Tschitschibatin[96] by the interaction of ethyl ortho-

formate and magnesium alkyl salts. Acetals are first obtained which, when hydrolysed, yield aldehydes:

$$H.C{\overset{\Large/OC_2H_5}{\underset{\Large\backslash OC_2H_5}{-OC_2H_5}}} + R.MgI = H.C{\overset{\Large/R}{\underset{\Large\backslash OC_2H_5}{-OC_2H_5}}} + Mg{\overset{\Large/OC_2H_5}{\underset{\Large\backslash I}{}}}$$

$$H.C{\overset{\Large/R}{\underset{\Large\backslash OC_2H_5}{-OC_2H_5}}} + H_2O + [HCl] = H.C{\overset{\Large/R}{\underset{\Large\backslash O}{}}} + 2C_2H_5OH + [HCl]$$
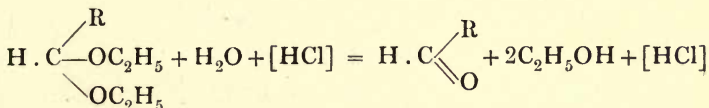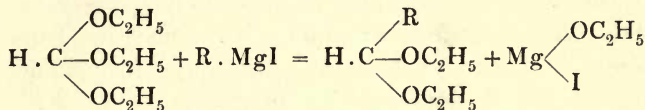
The yields of the various aldehydes so obtained differed greatly.

Shdanovitsch,[97] in a rather more complex instance, has obtained ethyl β-keto-$\delta\delta$-diethoxy-$\alpha\alpha\gamma\gamma$-tetra-methyl valerate as one of the products of the action of magnesium on a mixture of ethyl orthoformate and ethyl α-bromo*iso*butyrate:

$$H.C{\overset{\Large/OEt}{\underset{\Large\backslash OEt}{-|\,OEt}}} + BrMg.C{\overset{\Large Me}{\underset{\Large CO\,OEt}{|}}} + BrMg.C{\overset{\Large Me}{\underset{\Large COOEt}{|}}}$$

$$= 2Mg{\overset{\Large/OEt}{\underset{\Large\backslash Br}{}}} + {\overset{\Large H.C(OEt)_2}{\underset{\Large Me_2C.COOEt}{\underset{\Large |}{\overset{\Large |}{\overset{\Large CMe_2}{\underset{\Large |}{\overset{\Large |}{CO}}}}}}}$$
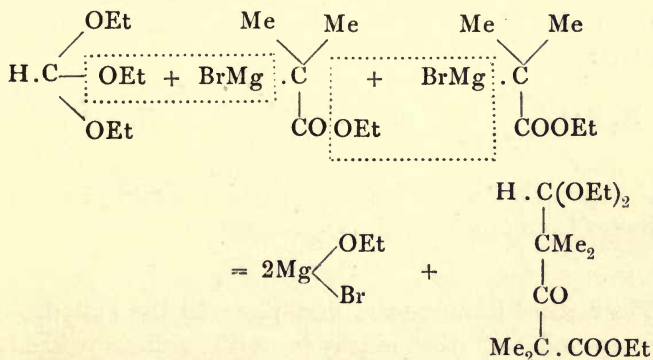
In the place of formic esters, the free acid in dilute

ethereal solution, or its copper salt, has been used in the preparation of aldehydes.[98]

Bouveault[99] has investigated the action of Grignard's reagents on disubstituted formamides, and obtained, for example, benzaldehyde from magnesium phenyl bromide and ethyl formamide. The reaction is expressed by the general equation:

$$H \cdot C {\overset{\displaystyle O}{\underset{\displaystyle NRR'}{\big\langle}}} + R''MgHal = H \cdot C {\overset{\displaystyle OMgHal}{\underset{\displaystyle NRR'}{\big\langle}}}\!\!-\!\!R''$$

$$H \cdot C {\overset{\displaystyle OMgHal}{\underset{\displaystyle NRR'}{\big\langle}}}\!\!-\!\!R'' + H_2O = H \cdot C {\overset{\displaystyle R''}{\underset{\displaystyle O}{\big\langle}}} + NHRR' + Mg(OH)Hal$$
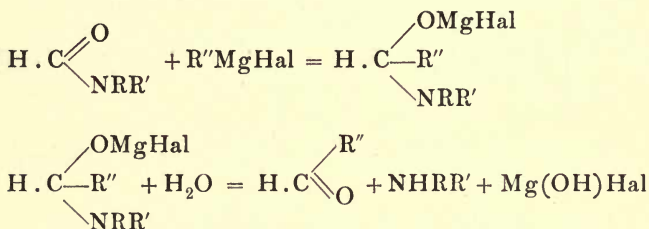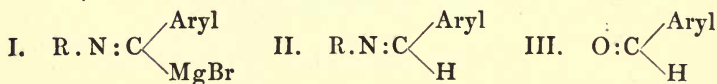
Isonitriles, according to Sachs and Loevy,[100] form addition compounds with organomagnesium salts (Formula I.), which, when treated with mineral acids, are converted into aldehyde-imide derivatives (Formula II.), and then into aldehydes (Formula III.):

$$\text{I.} \quad R \cdot N : C {\overset{\displaystyle Aryl}{\underset{\displaystyle MgBr}{\big\langle}}} \qquad \text{II.} \quad R \cdot N : C {\overset{\displaystyle Aryl}{\underset{\displaystyle H}{\big\langle}}} \qquad \text{III.} \quad O : C {\overset{\displaystyle Aryl}{\underset{\displaystyle H}{\big\langle}}}$$
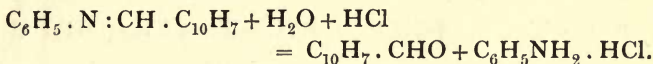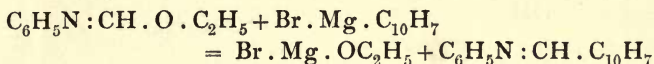
Monier-Williams[101] has prepared a series of aldehydes from ethoxymethyleneaniline,
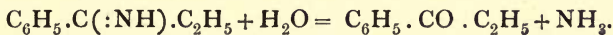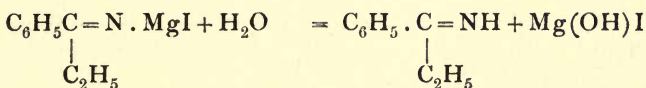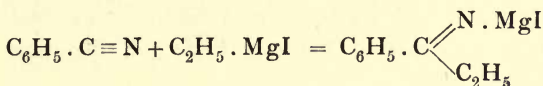
$$C_6H_5 \cdot N : CH \cdot OC_2H_5.$$
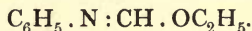
The method leads, in the first place, to the anhydro-compounds of the aldehyde with aniline which, when acted on by mineral acids, are hydrolysed to the aldehydes themselves and aniline. Thus,

α-naphthaldehyde was obtained in 48 per cent. yield from magnesium α-naphthyl bromide according to the equations:

$$C_6H_5N : CH . O . C_2H_5 + Br . Mg . C_{10}H_7$$
$$= Br . Mg . OC_2H_5 + C_6H_5N : CH . C_{10}H_7$$

$$C_6H_5 . N : CH . C_{10}H_7 + H_2O + HCl$$
$$= C_{10}H_7 . CHO + C_6H_5NH_2 . HCl.$$

Ketones.

Blaise[102] has succeeded in preparing ketones by the action of Grignard's reagents upon nitriles. Magnesium ethyl iodide and benzonitrile gave an 80 per cent. yield of phenyl ethyl ketone:

$$C_6H_5 . C \equiv N + C_2H_5 . MgI = C_6H_5 . C \begin{array}{c} N . MgI \\ \diagdown \\ C_2H_5 \end{array}$$

$$\underset{\overset{|}{C_2H_5}}{C_6H_5C = N . MgI} + H_2O = \underset{\overset{|}{C_2H_5}}{C_6H_5 . C = NH} + Mg(OH)I$$

$$C_6H_5 . C(:NH) . C_2H_5 + H_2O = C_6H_5 . CO . C_2H_5 + NH_3.$$

With nitriles of the type of benzyl cyanide,

$$C_6H_5 . CH_2CN,$$
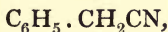
much poorer yields were obtained.

Similarly, varying yields of ketones were also obtained by Beis[103] by prolonged heating of acid amides with an excess of Grignard's reagents. On the probable assumption that the amide reacts in the enolic form,

$$R - C \begin{array}{c} NH \\ \diagdown \\ OH, \end{array}$$

the action may be represented in the following manner :

$$R.C \overset{\displaystyle NH}{\underset{\displaystyle OH}{<}} \ + 2R'MgHal = R.C \overset{\displaystyle NHMgHal}{\underset{\displaystyle OMgHal}{-R'}} \ + R'H$$

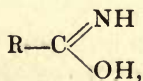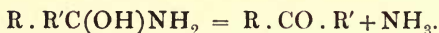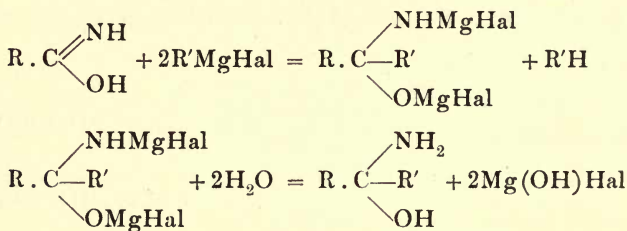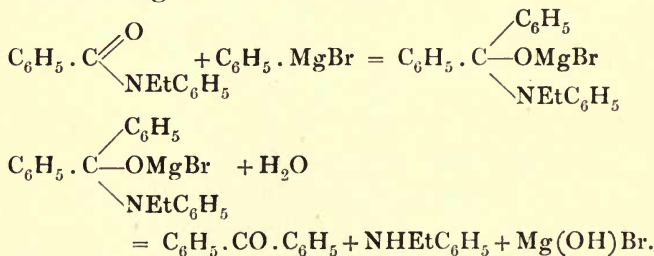$$R.C \overset{\displaystyle NHMgHal}{\underset{\displaystyle OMgHal}{-R'}} \ + 2H_2O = R.C \overset{\displaystyle NH_2}{\underset{\displaystyle OH}{-R'}} \ + 2Mg(OH)Hal$$

$$R.R'C(OH)NH_2 = R.CO.R' + NH_3.$$

An analogous reaction has been employed by McKenzie and Wren,[104] and by Wren,[105] in preparing r-, l-, and d- benzoin, $C_6H_5.CHOH.CO.C_6H_5$, from r-, l-, and d- mandelamide, $C_6H_5.CHOH.CO.NH_2$, respectively; and also by Ryan and Nolan,[106] for the production of a series of ketones from palmitamide and stearamide.

Busch and Fleischmann[107] found that magnesium phenyl bromide reacted with substituted anilides in the following manner:

$$C_6H_5.C \overset{\displaystyle O}{\underset{\displaystyle NEtC_6H_5}{<}} \ + C_6H_5.MgBr = C_6H_5.C \overset{\displaystyle C_6H_5}{\underset{\displaystyle NEtC_6H_5}{-OMgBr}}$$

$$C_6H_5.C \overset{\displaystyle C_6H_5}{\underset{\displaystyle NEtC_6H_5}{-OMgBr}} \ + H_2O$$

$$= C_6H_5.CO.C_6H_5 + NHEtC_6H_5 + Mg(OH)Br.$$

If, however, a second molecule of the reagent is used, a stable compound,

$$(C_6H_5)_3C.N \overset{\displaystyle C_2H_5}{\underset{\displaystyle C_6H_5,}{<}}$$
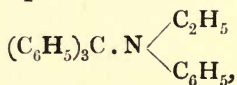
is formed.   The latter readily decomposes in alcoholic solution, with the formation of triphenylcarbinol and ethylaniline.

By the regulated action of Grignard's reagents upon acid chlorides it appears to be theoretically possible to prepare ketones:

$$R . COCl + R'MgHal = R . CO . R' + MgClHal.$$
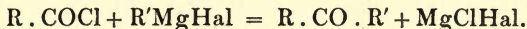
In general, however, this reaction does not appear to be easily controllable in such a manner that good yields of ketones are obtained.   Acree [108] has prepared phenyl a-naphthyl ketone, $C_6H_5 . CO . C_{10}H_7$, by the interaction of benzoyl chloride and magnesium a-naphthyl bromide under conditions which might be expected to lead to the production of phenyl di-a-naphthylcarbinol, whilst Gomberg and Cone [109] obtained a small yield of benzophenone from benzoyl chloride and magnesium phenyl bromide.   Further, Oddo [110] found that magnesium pyrryl iodide reacts with acyl chlorides with formation of ketones of the type

$$NH\Big\langle {\begin{matrix} CH = CH \\ | \\ C = CH \\ | \\ COR. \end{matrix}}$$
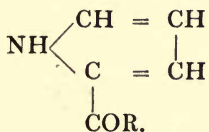
Ketones may also be produced under certain circumstances by the action of carbon dioxide on organomagnesium salts.   Schroeter [111] thus obtained benzophenone in small yield from magnesium phenyl bromide, and Bodroux [112] showed that ketones are the main product of the action of carbon dioxide on *warm* solutions of magnesium p-chlorophenyl bromide and

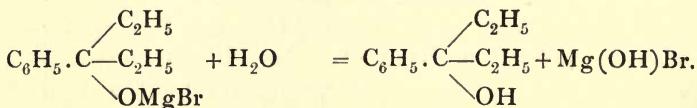magnesium p-bromophenyl bromide. v. Braun and
Sobecki [113] obtained *cyclo*pentanone by treating
magnesium butylene dibromide with carbon dioxide:

$$CH_2 . CH_2 . MgBr \\ | \qquad\qquad + CO_2 = \qquad CH_2 . CH_2 \\ CH_2 . CH_2 . MgBr$$

$$+ CO_2 = \begin{array}{c} CH_2 . CH_2 \\ | \qquad\qquad \diagdown CO + MgO + MgBr_2. \\ CH_2 . CH_2 \end{array}$$
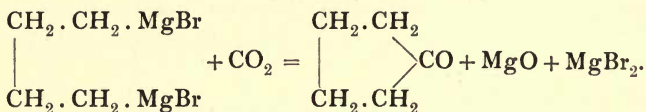
The action of magnesium organic compounds on
free acids has not been very extensively studied.
Since the main products formed are tertiary alcohols
and ketones, the results may be briefly considered in
this section. The first step in the reaction consists
in the replacement of the hydrogen of the carboxyl
group,

$$R' . COOH + R . MgHal = R' . COOMgHal + RH,$$
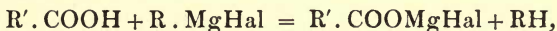
and the compound so formed is convertible by excess
of the reagent into tertiary alcohols and ketones
(compare the action of carbon dioxide on Grignard's
reagents, p. 26). Thus, benzoic acid can be converted
into diethylphenylcarbinol: [114]

$$C_6H_5 . C\diagup{\!\!\!\!\!}^O_{OH} + 2C_2H_5 . MgBr = C_6H_5 . C{\!\!-\!\!}C_2H_5\diagup{\!\!\!\!\!}^{OMgBr}_{OMgBr} + C_2H_6$$

$$C_6H_5 . C{\!\!-\!\!}C_2H_5\diagup{\!\!\!\!\!}^{OMgBr}_{OMgBr} + C_2H_5MgBr = C_6H_5 . C{\!\!-\!\!}C_2H_5\diagup{\!\!\!\!\!}^{C_2H_5}_{OMgBr} + MgO + MgBr_2$$

$$C_6H_5 . C{\!\!-\!\!}C_2H_5\diagup{\!\!\!\!\!}^{C_2H_5}_{OMgBr} + H_2O = C_6H_5 . C{\!\!-\!\!}C_2H_5\diagup{\!\!\!\!\!}^{C_2H_5}_{OH} + Mg(OH)Br.$$
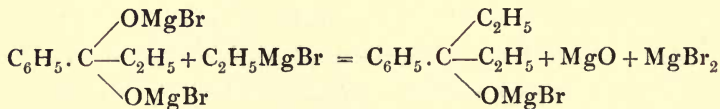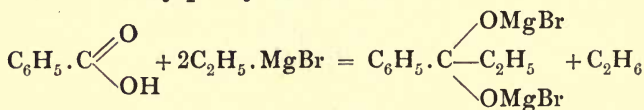
Whilst formic acid [115] yields aldehydes under the same conditions:

$$H . C\overset{O}{\underset{OH}{\diagdown}} + 2R . MgI = H . C\overset{R}{\underset{OMgI}{-OMgI}} + R . H$$

$$H . C\overset{R}{\underset{OMgI}{-OMgI}} + H_2O = H . C\overset{R}{\underset{O}{\diagdown}} + 2Mg(OH)I.$$
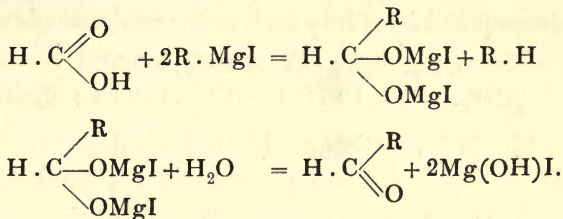
The production of ketones from acids has been investigated in the case of phthalic acid by Simonis and Arand,[116] who find that this substance, when acted on by excess of Grignard's reagents, yields two products, viz., a dialkyl phthalide and a ketone. Thus, phthalic acid and magnesium ethyl bromide gave diethylphthalide (Formula I.) and propiophenone-o-carboxylic acid (Formula II.):

$$\text{I.} \quad C_6H_4\overset{C(C_2H_5)_2}{\underset{CO}{\diagdown}}O \qquad \text{II.} \quad C_6H_4\overset{COC_2H_5}{\underset{COOH}{\diagdown}}$$
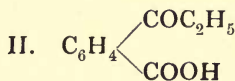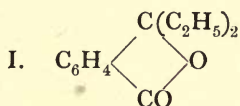
The analogous compound, naphthoyl-o-benzoic acid,

$$C_6H_4\overset{COC_{10}H_7}{\underset{COOH,}{\diagdown}}$$
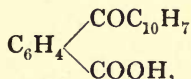
has been prepared by Pickles and Weizmann [117] by the interaction of magnesium a-naphthyl bromide and phthalic anhydride.

Acids.

Carboxylic acids were prepared by Grignard,[118] who showed that solutions of magnesium organic halides readily absorb carbon dioxide. Thus, when

dry carbon dioxide was passed into an ethereal solution of magnesium methyl iodide and the product decomposed by dilute acid, acetic acid was obtained:

$$CH_3 . MgI + CO_2 = CH_3 . CO_2MgI$$
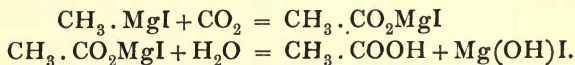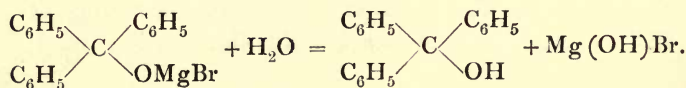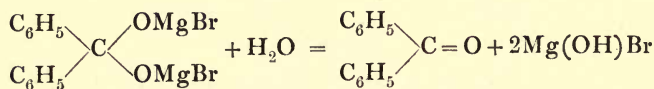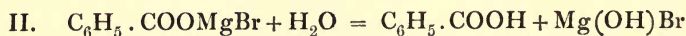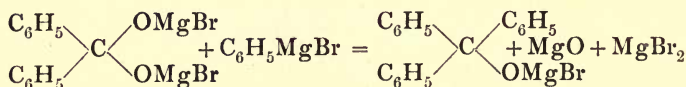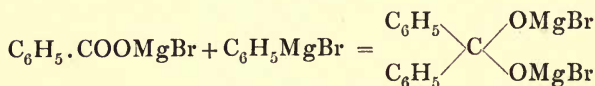$$CH_3 . CO_2MgI + H_2O = CH_3 . COOH + Mg(OH)I.$$

Similarly, Zelinsky obtained a 60 per cent. yield of benzoic acid from magnesium phenyl iodide,[119] and Schmidlin[120] prepared triphenylacetic acid, $(C_6H_5)_3CCOOH$, in good yield by the decomposition of magnesium triphenylmethyl chloride, $(C_6H_5)_3C . MgCl$, by carbon dioxide.

Schroeter[121] substituted magnesium phenyl bromide for the iodide when a more complex change occurred whereby benzoic acid, benzophenone, and triphenylcarbinol were obtained. The course of the reaction may be represented by the equations:

I. $C_6H_5 . MgBr + CO_2 = C_6H_5 . COOMgBr$

$$C_6H_5 . COOMgBr + C_6H_5MgBr = \begin{matrix} C_6H_5 \\ \diagdown \\ C_6H_5 \diagup \end{matrix} C \begin{matrix} \diagup OMgBr \\ \diagdown OMgBr \end{matrix}$$

$$\begin{matrix} C_6H_5 \\ \diagdown \\ C_6H_5 \diagup \end{matrix} C \begin{matrix} \diagup OMgBr \\ \diagdown OMgBr \end{matrix} + C_6H_5MgBr = \begin{matrix} C_6H_5 \\ \diagdown \\ C_6H_5 \diagup \end{matrix} C \begin{matrix} \diagup C_6H_5 \\ \diagdown OMgBr \end{matrix} + MgO + MgBr_2$$

II. $C_6H_5 . COOMgBr + H_2O = C_6H_5 . COOH + Mg(OH)Br$

$$\begin{matrix} C_6H_5 \\ \diagdown \\ C_6H_5 \diagup \end{matrix} C \begin{matrix} \diagup OMgBr \\ \diagdown OMgBr \end{matrix} + H_2O = \begin{matrix} C_6H_5 \\ \diagdown \\ C_6H_5 \diagup \end{matrix} C = O + 2Mg(OH)Br$$

$$\begin{matrix} C_6H_5 \\ \diagdown \\ C_6H_5 \diagup \end{matrix} C \begin{matrix} \diagup C_6H_5 \\ \diagdown OMgBr \end{matrix} + H_2O = \begin{matrix} C_6H_5 \\ \diagdown \\ C_6H_5 \diagup \end{matrix} C \begin{matrix} \diagup C_6H_5 \\ \diagdown OH \end{matrix} + Mg(OH)Br.$$

Later,[122] the same author showed that the experimental conditions may be so adjusted that no benzoic acid is formed, and that the production of the latter depended upon the quantity of carbon dioxide employed and the temperature at which the gas was passed into the ethereal solution.[123] In this connection it is interesting to note that Grignard[124] has prepared trialkylcarbinols by saturating a solution of alkyl magnesium halide with carbon dioxide, and protracted heating of the compound so formed with two additional molecules of the organomagnesium salt (see p. 26); and further, that Bodroux[125] has observed that carbon dioxide transforms magnesium p-chloro- and p-bromophenyl bromide at a higher temperature chiefly into dichloro- and dibromo- benzophenone, at a lower temperature, however, into the corresponding substituted benzoic acids.

Oddo[126] found that a small amount of propiolic acid was formed when magnesio-acetylene bromide was treated with carbon dioxide followed by dilute sulphuric acid:

$$HC \equiv C \cdot MgBr + CO_2 = H \cdot C \equiv C \cdot CO_2MgBr$$

$$2H \cdot C \equiv C \cdot CO_2MgBr + H_2O + H_2SO_4$$
$$= 2H \cdot C \equiv C \cdot COOH + MgBr_2 + MgSO_4 + H_2O.$$
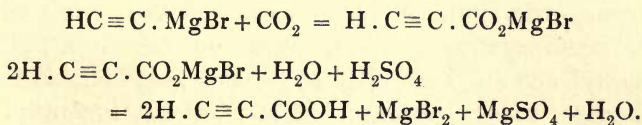
Houben and Pohl[127] have shown that carbithionic acids are formed when carbon disulphide is substituted for carbon dioxide in the above reactions. Thus, when carbon disulphide was added to a cooled solution of magnesium methyl iodide in absolute ether and the product decomposed with ice and cooled

hydrochloric acid, dithioacetic acid, $CH_3 . CSSH$, was obtained as an unstable, reddish-yellow oil.

Hydroxy-acids have been obtained by the action of Grignard's reagents upon ketonic esters followed by saponification of the product so formed. A ketonic ester presents two points of attack to the Grignard reagent, viz., the carbonyl group and the carbalkoxy group, but, by careful regulation of the relative quantities of ester and re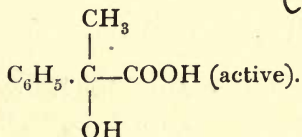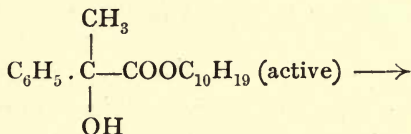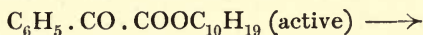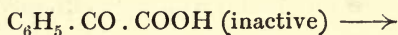agent employed, and by so conducting the experiment that the latter is never in excess, it is possible to limit the action completely, or almost completely, to the carbonyl group. Grignard[128] has prepared a series of hydroxy-acids in this manner,

$$R . CO \ldots CO . OC_2H_5 + R'MgI \longrightarrow \begin{matrix} R \\ \diagdown \\ \diagup \\ R' \end{matrix} C(OH) \ldots CO . OC_2H_5,$$
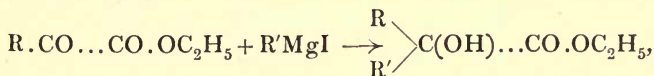
but the reaction cannot be applied to β-ketonic esters which possess the ability to pass into an enolic form.

In a similar manner, the reaction has been extensively employed in the investigation of the problem of asymmetric synthesis by McKenzie,[129] the action of various organomagnesium salts on the menthyl, bornyl, and amyl esters of a-, β-, and γ- ketonic acids having been examined. Thus, when l-menthyl benzoylformate was acted on by magnesium methyl iodide, a mixture of unequal amounts of l-menthyl d-phenylmethylglycollate and l-menthyl l-phenyl-methylglycollate was produced, and when this mixture was saponified by an excess of alkali and the resulting menthol completely removed, the potassium salt formed was optically active, as also was the acid

obtained from it. The asymmetric synthesis of an optically active phenylmethylglycollic acid (atro-lactinic acid) had therefore been accomplished in accordance with the scheme:

$$C_6H_5 . CO . COOH \text{ (inactive)} \longrightarrow$$
$$C_6H_5 . CO . COOC_{10}H_{19} \text{ (active)} \longrightarrow$$

$$\begin{matrix} & CH_3 & \\ & | & \\ C_6H_5 . & C\!\!-\!\!COOC_{10}H_{19} \text{ (active)} \longrightarrow \\ & | & \\ & OH & \end{matrix}$$

$$\begin{matrix} & CH_3 & \\ & | & \\ C_6H_5 . & C\!\!-\!\!COOH \text{ (active).} \\ & | & \\ & OH & \end{matrix}$$

Oddo[130] has investigated the behaviour of carbon dioxide towards the iodo-magnesium derivatives of various phenols which can undergo conversion into the corresponding hydroxy-acids (according to Kolbe's synthesis of aromatic hydroxy-acids from sodium aryloxides by means of carbon dioxide). With the phenol and resorcinol derivatives this change only occurred in the absence of solvent, and at a somewhat elevated temperature. With derivatives of the following phenols the reaction proceeded in the presence of a solvent (benzene or toluene): β-naphthol, which yielded β-naphthol-α-carboxylic acid; phloro-glucinol, giving phloroglucinol carboxylic acid; thymol, giving o-thymotic acid

$$[CH_3 : CO_2H : OH : C_3H_7 = 1 : 2 : 3 : 4].$$
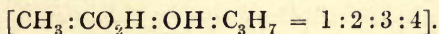
An interesting synthesis of aromatic amino-acids by rearrangement has been accomplished by Houben and Schottmüller [131] by treatment of methylaniline, methyl iodide, and magnesium with dry carbon dioxide. Reaction was found to proceed in accordance with the equation:

$$C_6H_5NHCH_3 + CO_2 + CH_3I + Mg = CH_4 + C_6H_5N\begin{matrix} \diagup CH_3 \\ \diagdown COOMgI \end{matrix}$$
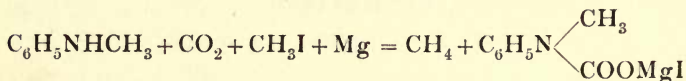
The latter compound underwent rearrangement with the formation of the substance,
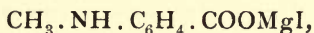
$$CH_3 . NH . C_6H_4 . COOMgI,$$

from which an almost quantitative yield of p-mono-methylaminobenzoic acid, $CH_3 . NH . C_6H_4 . COOH$, was obtained. Methylaniline, in this reaction, may be replaced by a mixture of aniline and dimethyl-aniline, whilst dimethylaniline hydroiodide may be used in place of a mixture of methylaniline and methyl iodide.

The action of sulphur dioxide on an ethereal solution of an organomagnesium salt leads, according to Rosenheim and Singer,[132] to the formation of sulphinic acids, the yields being 50 to 60 per cent. of the theoretical. Thus, phenyl magnesium bromide and sulphur dioxide yielded phenyl sulphinic acid:

$$C_6H_5 . MgBr + SO_2 = C_6H_5 . SO_2 . MgBr$$

$$C_6H_5 . SO_2 . MgBr + H_2O = C_6H_5 . SO_2H + Mg(OH)Br.$$
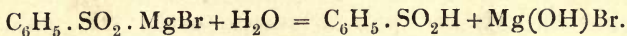
As by-product, diphenyl sulphoxide, $(C_6H_5)_2SO$, was

obtained. The authors, however, point out that reduction and transformation of the sulphinic acids so formed readily takes place. This fact probably accounts for the circumstance that Oddo[133] finds that phenyl sulphide, small quantities of phenyl sulphoxide and diphenyl, are the products of inter-action of the same two substances.

Houben prepared dihydropinenesulphinic acid by the action of sulphur dioxide on magnesium pinyl chloride, $C_{10}H_{17} . MgCl$.

The replacement of sulphur dioxide by thionyl chloride in the above reactions led to the production of sulphoxides and sulphides. Thus, magnesium ethyl iodide yielded ethyl sulphide, magnesium phenyl bromide gave phenyl sulphide in addition to small quantities of phenyl sulphoxide and diphenyl.[134] Similarly, Strecker[135] obtained benzyl sulphoxide and benzyl sulphide by the action of magnesium benzyl bromide on thionyl chloride. The former compound was also obtained when magnesium benzyl bromide acted on symmetrical diethyl sulphite, whereas phenylethylsulphone resulted from the inter-action of magnesium phenyl bromide and unsym-metrical diethyl sulphite.

Esters.

Numerous syntheses of esters are recorded, based upon the action of Grignard's reagents with ethyl carbonate and closely allied compounds. Houben[136] found that when magnesium phenyl bromide was added to ethyl chlorocarbonate, $Cl . COOC_2H_5$, in such

a manner that excess of the former was avoided, ethyl benzoate was obtained:

$$C_6H_5 . MgBr + Cl . COOC_2H_5$$
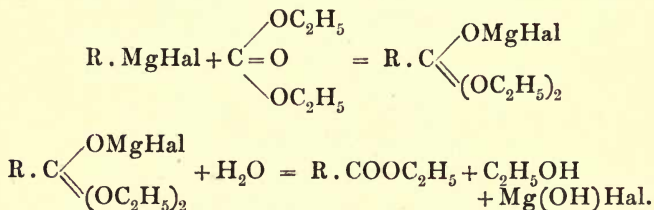$$= C_6H_5 . COOC_2H_5 + MgBrCl.$$
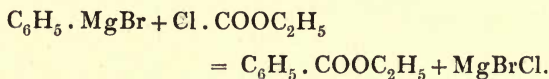
Tschitschibabin [137] obtained varying yields of esters by the interaction of organomagnesium compounds and ethyl carbonate. The reaction appears to proceed in accordance with the equation:

$$R . MgHal + C \overset{OC_2H_5}{\underset{OC_2H_5}{\diagdown}} = R . C \overset{OMgHal}{\underset{(OC_2H_5)_2}{\diagdown}}$$

$$R . C \overset{OMgHal}{\underset{(OC_2H_5)_2}{\diagdown}} + H_2O = R . COOC_2H_5 + C_2H_5OH + Mg(OH)Hal.$$

The yields are stated to be considerably improved if air is excluded during the reaction by means of a current of dry hydrogen.

The same author [138] found that the regulated action of orthocarbonic esters on organomagnesium compounds led to the production of ortho-esters, from which, by the action of acids, the normal esters could be obtained:

$$C(OC_2H_5)_4 + R . MgHal = R . C(OC_2H_5)_3 + Mg(OC_2H_5)Hal$$
$$R . C(OC_2H_5)_3 + H_2O = R . COOC_2H_5 + 2C_2H_5OH.$$
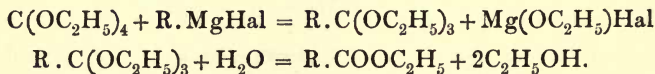
An interesting method for the preparation of esters from alcohols and phenols is described by Houben. [139] It depends upon the decomposition of

a suitable Grignard's reagent by the alcohol (or phenol),

$$R.OH + R'MgCl = R.O.MgCl + R'H,$$
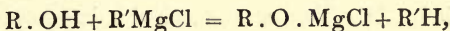
and subsequent addition of acetic anhydride (or, less frequently, of acetyl chloride) to the product so formed :

$$R.O.MgCl + (CH_3CO)_2O$$
$$= R.O.COCH_3 + CH_3.COOMgCl.$$

In this manner a large number of alcohols were converted into esters, the yield being generally excellent. Houben concludes that alkyl bromo- and iodo-magnesium alcoholates are only suitable when saturated alcohols and, possibly, phenols are to be esterified, whereas chloromagnesium alcoholates can be employed with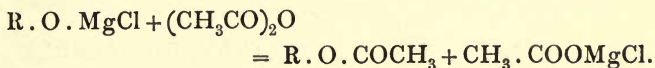 satisfactory results even with unstable and unsaturated alcohols and phenols; and, further, that polyhydroxy and solid, sparingly soluble alcohols can be esterified in this manner.

Esters of ketonic acids have been prepared by Meyer and Tögel [140] by the action of acid chlorides on the magnesium compounds of halogenated esters. Thus, ethyl benzoylacetate, $C_6H_5.CO.CH_2.COOC_2H_5$, was obtained by adding benzoyl bromide to magnesium ethyl bromoacetate :

$$C_6H_5COBr + BrMg.CH_2.COOC_2H_5$$
$$= C_6H_5.CO.CH_2.COOC_2H_5 + MgBr_2.$$
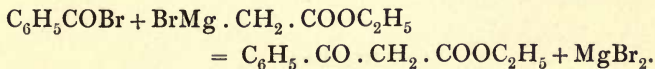
Ethyl acetoacetate, ethyl α-benzoylpropionate, and ethyl β-benzoylpropionate were formed in an analogous manner.

Zeltner[141] has obtained esters of β-ketonic acids by the action of magnesium on the esters of α-halogen fatty acids. In this manner, ethyl α-bromopropionate gave a 35 per cent. yield of ethyl α-propionylpropionate, $CH_3 . CH . (CO . CH_2 . CH_3) . COOC_2H_5$.

$$CH_3.CHBr.COOC_2H_5 + Mg = CH_3.CH(MgBr).COOC_2H_5$$

$$CH_3 . CH(MgBr) . C\underset{\displaystyle OC_2H_5}{\overset{\displaystyle O}{\big<}} + CH_3 . CH(MgBr) . COOC_2H_5$$

$$= CH_3 . CH(MgBr) . C\underset{\displaystyle OC_2H_5}{\overset{\displaystyle OMgBr}{\big<}}\!\!-\!CHCH_3 . COOC_2H_5$$

$$CH_3 . CH(MgBr) . C\underset{\displaystyle OC_2H_5}{\overset{\displaystyle OMgBr}{\big<}}\!\!-\!CHCH_3 . COOC_2H_5 + 2H_2O$$

$$= CH_3 . CH_2 . C\underset{\displaystyle OC_2H_5}{\overset{\displaystyle OH}{\big<}}\!\!-\!CHCH_3 . COOC_2H_5 + 2Mg(OH)Br$$

$$CH_3 . CH_2 . C\underset{\displaystyle OC_2H_5}{\overset{\displaystyle OH}{\big<}}\!\!-\!CHCH_3 . COOC_2H_5$$

$$= CH_3 . CH_2 . CO . CH(CH_3)COOC_2H_5 + C_2H_5OH.$$
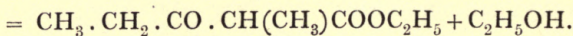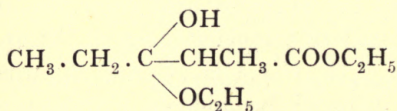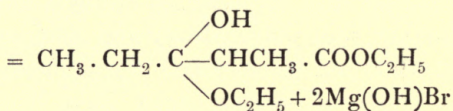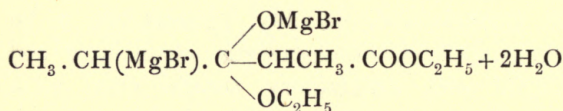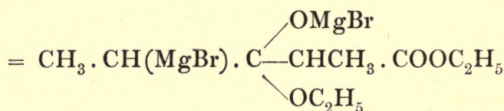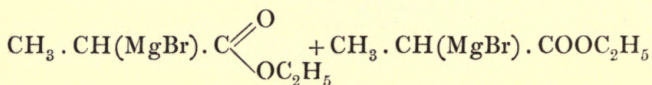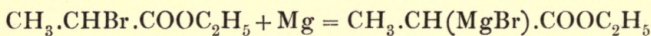
Nitriles.

Two methods of preparing nitriles with the aid of magnesium organic salts have recently been proposed by Grignard.[142] The first consists in the cautious

addition of ethereal solutions of magnesium alkyl halides to an ethereal solution of cyanogen chloride,

$$R . MgHal + Cl . CN = R . CN + Mg(Hal)Cl.$$
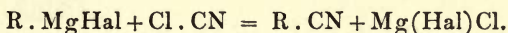
The yields obtained are satisfactory.

Cyanogen bromide and iodide are not suitable for this purpose; with the latter, reaction proceeds entirely in accordance with the equation,

$$R . MgBr + CNI = RI + MgBrCN,$$
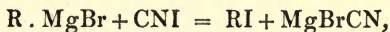
whilst, with cyanogen bromide, reactions of both types occur, the latter preponderating.

The second method consists in substituting cyanogen itself for its halogen derivative. It has been used to prepare benzonitrile, *iso*hexonitrile, and phenyl-butyronitrile, but the yields are inferior to those obtained with cyanogen chloride. If cyanogen or its chloride is added to the solution of the organo-magnesium compound, ketones are produced in the usual manner.

According to Grignard and Bellet,[143] alkyl cyclic nitriles can be prepared by adding the corresponding magnesium alkyl bromide drop by drop to a cold ethereal solution of cyanogen. In this manner, cyanohexamethylene, *o*-, *m*-, and *p*-methyl*cyclo*hexane-carboxylonitriles have been obtained.

Cyanuric chloride and magnesium phenyl bromide react in ethereal solution with the successive production of dichlorophenyltriazine, $C_3N_3Cl_2C_6H_5$, and chlorodiphenyltriazine, $C_3N_3Cl(C_6H_5)_2$.[144]

Nitrogen Compounds.

Aromatic amides have been obtained by Blaise [145]

by the action of organomagnesium compounds on aryl carbimides:

$$C_6H_5N = C = O + R.MgI = C_6H_5.N = C\begin{smallmatrix} OMgI \\ R \end{smallmatrix}$$

$$C_6H_5.N = C\begin{smallmatrix} OMgI \\ R \end{smallmatrix} + H_2O = C_6H_5NH.CO.R + Mg(OH)I.$$
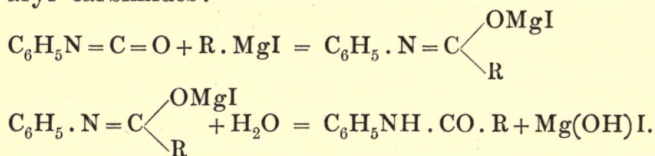
By a precisely similar reaction, Sachs and Loevy [146] have prepared thioanilides from mustard oils. Phenyl mustard oil and magnesium benzyl bromide yielded the anilide of thiophenylacetic acid,

$$C_6H_5.CH_2.CS.NHC_6H_5:$$

$$C_6H_5.N = C = S + C_6H_5CH_2.MgBr$$
$$= C_6H_5.N:C\begin{smallmatrix} CH_2C_6H_5 \\ SMgBr \end{smallmatrix}$$

$$C_6H_5.N = C\begin{smallmatrix} CH_2.C_6H_5 \\ S.MgBr \end{smallmatrix} + H_2O$$
$$= C_6H_5.NH.CS.CH_2C_6H_5 + Mg(OH)Br.$$
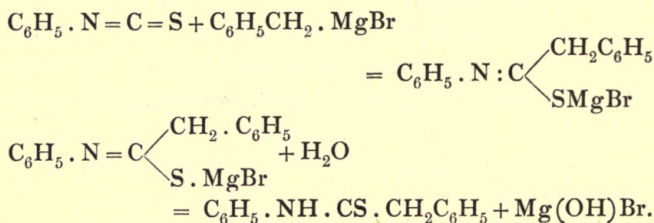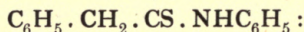
Anilides have also been obtained by Bodroux [147] by treatment of the compounds formed by the action of magnesium organic halides on primary amines (of the type $R.NH.MgHal$) with the ester of a monobasic acid and subsequent decomposition of this product by means of dilute acid:

$$R.NH_2 + X.MgHal = R.NH.MgHal + XH$$

$$2R.NHMgHal + R'.C\begin{smallmatrix} O \\ OR'' \end{smallmatrix} = R'.C\begin{smallmatrix} OMgHal \\ NHR \\ NHR \end{smallmatrix} + Mg(OR'')Hal$$

$$R'.C\begin{smallmatrix} O.MgHal \\ (NHR)_2 \end{smallmatrix} + HCl = R.NH_2 + R_1.CO.NHR + Mg(Hal)Cl.$$
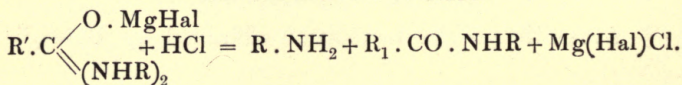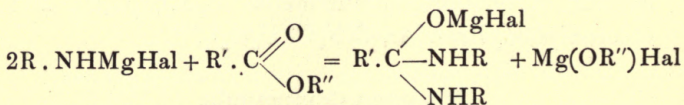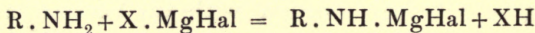
The same author [148] found that a substituted urethane was obtained when ethyl carbonate was substituted for the ester of a monobasic acid in the above reaction:

$$C=O \begin{array}{c} OC_2H_5 \\ OC_2H_5 \end{array} + 2R.NH.MgI = \begin{array}{c} NHR \\ | \\ C \\ | \\ OC_2H_5 \end{array} \begin{array}{c} NHR \\ OMgI \end{array} + Mg(OC_2H_5)I$$

$$C \begin{array}{c} (NHR)_2 \\ OMgI \\ OC_2H_5 \end{array} + H_2O = C \begin{array}{c} (NHR)_2 \\ OH \\ OC_2H_5 \end{array} + Mg(OH)I$$

$$\begin{array}{c} NHR \\ | \\ C \\ | \\ OC_2H_5 \end{array} \begin{array}{c} NHR \\ OH \end{array} = C=O \begin{array}{c} NHR \\ OC_2H_5 \end{array} + NH_2R.$$
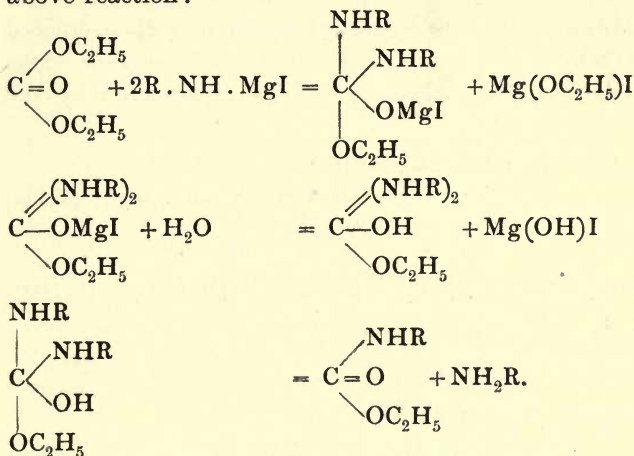
Busch and Rinck [149] have succeeded in transforming alkylidene bases into secondary amines by means of Grignard's reagents. Thus, C-ethylbenzylaniline was obtained from magnesium ethyl iodide and benzylidene aniline:

$$\begin{array}{c} C_6H_5.N \\ \| \\ C_6H_5.CH \end{array} + C_2H_5.MgI = \begin{array}{cc} C_6H_5.N——CH.C_6H_5 \\ | \quad\quad | \\ MgI \quad C_2H_5 \end{array}$$

$$\begin{array}{cc} C_6H_5.N——CH.C_6H_5 + H_2O \\ | \quad\quad | \\ MgI \quad C_2H_5 \end{array}$$
$$= C_6H_5.NH.CH(C_2H_5).C_6H_5 + Mg(OH)I.$$
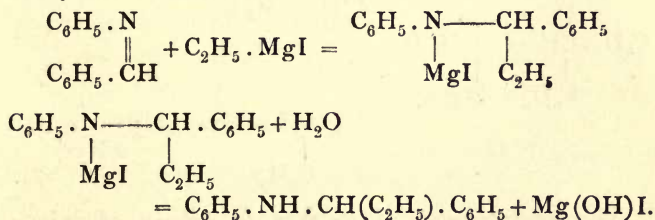
The interaction of oximes and organomagnesium salts has been investigated by Busch and Hobein [150]

in the expectation that addition of the reagents would take place at the $=C=N-$ linkage in the same manner as with alkylidene bases. This was found to be the case, but the process was not limited to this addition, since the hydroxyl group was also replaced by alkyl. In some cases the second reaction alone occurred. The whole process is represented by the equations:

$$R \cdot CH = N \cdot OH + 2R' \cdot MgHal$$

$$= \underset{\underset{R'}{\mid}\ \underset{MgHal}{\mid}}{R \cdot CH - N - R'} + Mg(OH)Hal$$

$$\underset{\underset{R'}{\mid}\ \underset{MgHal}{\mid}}{R \cdot CH - N - R'} + H_2O = \underset{\underset{R'}{\mid}}{R \cdot CH - NHR'} + Mg(OH)Hal.$$
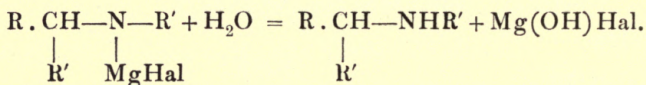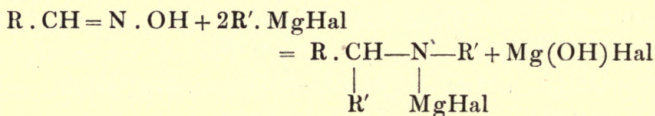
Thus, a-benzaldoxime and magnesium phenyl bromide yielded diphenylanilidomethane,

$$(C_6H_5)_2 \cdot CH \cdot NHC_6H_5.$$
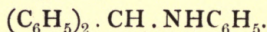
The same products were obtained when O-ethers of oximes were substituted for the simple oximes:

$$C_6H_5 \cdot CH : N \cdot OCH_3 + 2C_6H_5 \cdot MgBr$$

$$= \underset{\underset{C_6H_5}{\mid}\ \underset{MgBr}{\mid}}{C_6H_5 \cdot CH \text{——} N \cdot C_6H_5} + Mg(OCH_3)Br$$

$$\underset{\underset{C_6H_5}{\mid}\ \underset{MgBr}{\mid}}{C_6H_5 \cdot CH \text{——} N \cdot C_6H_5} + H_2O$$

$$= \underset{\underset{C_6H_5}{\mid}}{C_6H_5 \cdot CH - NH \cdot C_6H_5} + Mg\begin{smallmatrix}OH\\Br.\end{smallmatrix}$$
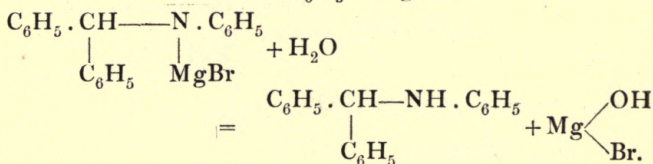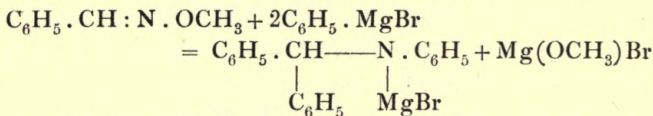
The replacement of oximes or ethers of oximes in the above reaction by β-phenylhydroxylamine [151] led to unexpected results. This compound was

converted by magnesium phenyl bromide into triphenylhydrazine, azobenzene being possibly formed as an intermediate product and reacting with the organomagnesium salt, thus:

$$C_6H_5 . N = N . C_6H_5 + C_6H_5 . MgBr = C_6H_5 . N\underset{\underset{C_6H_5}{|}}{\qquad} N\underset{\underset{MgBr}{|}}{} C_6H_5$$

$$C_6H_5 . N\underset{\underset{C_6H_5}{|}}{\qquad} N\underset{\underset{MgBr}{|}}{} . C_6H_5 + H_2O$$

$$= C_6H_5 . N\underset{\underset{C_6H_5}{|}}{\qquad} N\underset{\underset{H}{|}}{} . C_6H_5 + Mg(OH)Br.$$
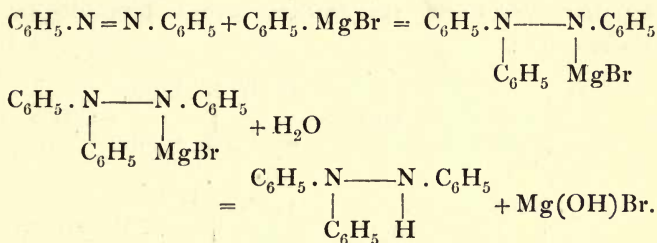
Or, more probably, the phenylhydroxylamine is partly transformed into diphenylamine, which then condenses with an additional molecule of phenyl-hydroxylamine,

$$(C_6H_5)_2NH + OH . NHC_6H_5 = (C_6H_5)_2N . NHC_6H_5 + H_2O.$$

$\beta\beta$-Dialkylhydroxylamines, R_2NOH, have been obtained by Wieland[152] by the action of nitrogen peroxide upon magnesium alkyl halides, the nitrogen being reduced from the tetravalent to the trivalent condition. An attempt to obtain similar compounds from magnesium aryl halides was unsuccessful.[153]
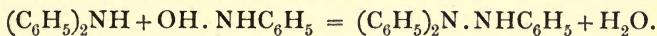
Nitric oxide reacts with magnesium alkyl salts with the formation of nitrosoalkylhydroxylamines, according to the scheme:[154]

$$NO \longrightarrow O = N - N = O \longrightarrow O = N - N\begin{cases} O . MgBr \\ C_2H_5 \end{cases}$$

$$\longrightarrow O = N - N\begin{cases} OH \\ C_2H_5 \end{cases}$$
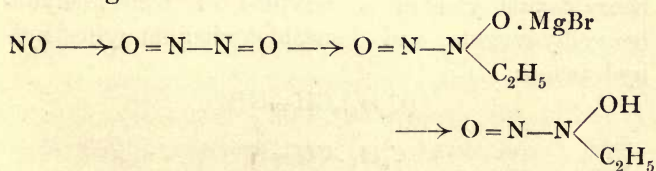
An interesting case, in which magnesium alkyl salts appear to function as reducing agents, has been examined by Franzen and Diebel,[155] who find that a good yield of hydrazobenzene may be obtained by the action of magnesium ethyl bromide on azobenzene:

$$\begin{array}{c} C_6H_5.N \\ \| \\ C_6H_5.N \end{array} + 2C_2H_5.MgBr = \begin{array}{c} C_6H_5.N.MgBr \\ | \\ C_6H_5.N.MgBr \end{array} + C_4H_{10}$$

$$\begin{array}{c} C_6H_5.N.MgBr \\ | \\ C_6H_5.N.MgBr \end{array} + 2H_2O = \begin{array}{c} C_6H_5.NH \\ | \\ C_6H_5.NH \end{array} + 2Mg(OH)Br$$
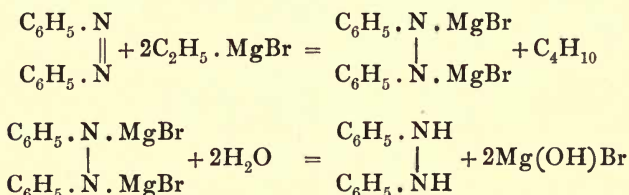
In a somewhat similar manner, benzaldazine is reduced to benzaldehydebenzylhydrazone:
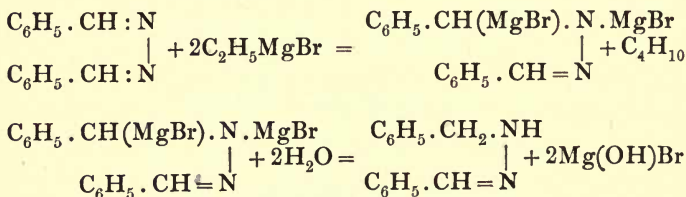
$$\begin{array}{c} C_6H_5.CH:N \\ | \\ C_6H_5.CH:N \end{array} + 2C_2H_5MgBr = \begin{array}{c} C_6H_5.CH(MgBr).N.MgBr \\ | \\ C_6H_5.CH=N \end{array} + C_4H_{10}$$

$$\begin{array}{c} C_6H_5.CH(MgBr).N.MgBr \\ | \\ C_6H_5.CH=N \end{array} + 2H_2O = \begin{array}{c} C_6H_5.CH_2.NH \\ | \\ C_6H_5.CH=N \end{array} + 2Mg(OH)Br$$

Busch and Fleischmann[156] find that, in addition to this reaction, which may even proceed to the extent of forming dibenzylhydrazine, the normal addition also occurs. Thus, magnesium phenyl bromide and benzaldazine yielded a mixture of benzaldehyde-benzylhydrazone and benzaldehydediphenylmethyl-hydrazone:

$$\begin{array}{c} (C_6H_5)_2CH\text{---}NH \\ | \\ C_6H_5.CH=N \end{array}$$
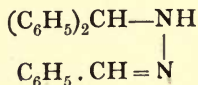
The action of organomagnesium salts on quaternary ammonium halides, which react with alkali to form pseudobases, has been investigated by Freund and his co-workers,[157] who find that they yield substances which differ from the pseudobases by containing a hydrocarbon residue in place of the hydroxyl group. The action of magnesium ethyl bromide on quinoline methiodide may be considered as typical. It leads to the formation of 1-methyl-2-ethyldihydroquinoline:
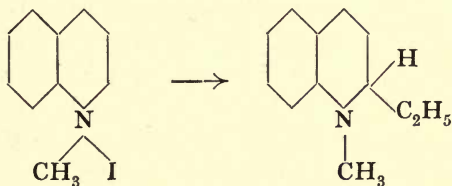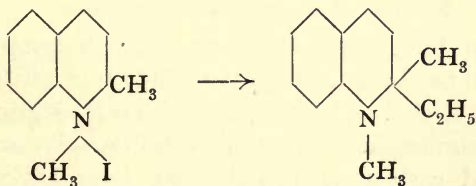

Addition likewise occurs even if the hydrogen atom in position 2 is replaced by an alkyl group: 2-methylquinoline methiodide and magnesium ethyl bromide yielded 1:2-dimethyl-2-ethyldihydroquinoline:

Dimroth[158] has utilised organomagnesium salts in the preparation of diazoamino-compounds. Thus, diazoaminomethane (dimethyltriazine) was obtained by leading a current of methylazoimide into a well-cooled, ethereal solution of magnesium methyl iodide

and decomposing the product by means of a concentrated aqueous solution of ammonium chloride :

$$CH_3 . MgI + N \underset{N}{\overset{\|}{\diagdown}} N . CH_3 = \underset{MgI}{\overset{CH_3 . N = N . N . CH_3}{|}}$$

$$\underset{MgI}{\overset{CH_3 . N = N . N . CH_3}{|}} + H_2O = CH_3 . N = N . NHCH_3 + Mg(OH)I$$

The interaction of organomagnesium salts and nitro-compounds does not appear to have been very thoroughly examined. Nitrobenzene, ethyl iodide, and magnesium react in benzene solution with the formation of phenylethylamine and azobenzene. Nitroethane and amyl nitrite, according to Mouren,[159] are converted by magnesium ethyl iodide into diethylhydroxylamine.

Strecker[160] finds that neither magnesium ethyl iodide nor magnesium phenyl bromide reacts with nitrogen trichloride dissolved in benzene.

Formation of Additive Compounds by Means of Grignard's Reagents.

In the foregoing section on nitrogen compounds, reference has been made to the addition of Grignard's reagents to the —C=N— and —N=N— groups.

The interaction of organomagnesium salts and unsaturated carbon compounds has been extensively investigated by Kohler and his co-workers,[161] who find that, in the case of $\alpha\beta$ unsaturated ketones, the course of the reaction depends upon the nature of the ketone. If the latter contains the methyl group attached to the carbonyl group, it reacts as a

saturated ketone, and the final product is a tertiary alcohol; if, however, a phenyl group is next the carbonyl group, addition of the magnesium alkyl salt occurs in the $a\delta$ position, and a ketone results:

$$\text{I.} \quad C_6H_5 . CH = CH—C \underset{\displaystyle \diagdown O}{\overset{\displaystyle \diagup CH_3}{}} + R . MgHal$$

$$= C_6H_5 . CH = CH—C \underset{\displaystyle \diagdown R}{\overset{\displaystyle \diagup CH_3}{—OMgHal}}$$

$$C_6H_5 . CH = CH—C \underset{\displaystyle \diagdown R}{\overset{\displaystyle \diagup CH_3}{—OMgHal}} + H_2O$$
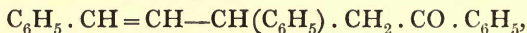
$$= C_6H_5 . CH = CH—C \underset{\displaystyle \diagdown R}{\overset{\displaystyle \diagup CH_3}{—OH}} + Mg(OH)Hal.$$

$$\text{II.} \quad C_6H_5 . CH = CH—C \underset{\displaystyle \diagdown O}{\overset{\displaystyle \diagup C_6H_5}{}} + R . MgHal$$

$$= C_6H_5 . \underset{\displaystyle \overset{\displaystyle |}{R}}{CH}—CH = C \underset{\displaystyle \diagdown OMgHal}{\overset{\displaystyle \diagup C_6H_5}{}}$$

$$C_6H_5 . \underset{\displaystyle \overset{\displaystyle |}{R}}{CH}—CH = C \underset{\displaystyle \diagdown OMgHal}{\overset{\displaystyle \diagup C_6H_5}{}} + H_2O$$

$$= C_6H_5 . \underset{\displaystyle \overset{\displaystyle |}{R}}{CH} . CH_2 . CO . C_6H_5 + Mg(OH)Hal.$$
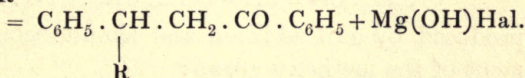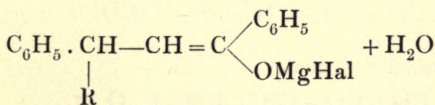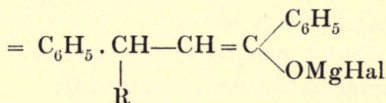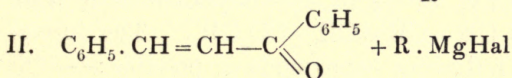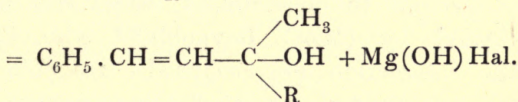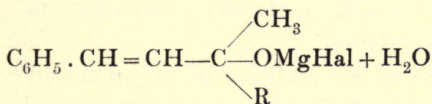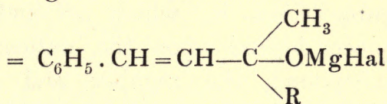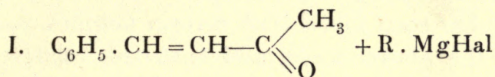
Doubly unsaturated ketones containing the group —C = C—C = C— behave similarly. Thus, cinnamyl-ideneacetophenone,

$$C_6H_5 . CH = CH—CH = CH . C \underset{\displaystyle \diagdown O,}{\overset{\displaystyle \diagup C_6H_5}{}}$$
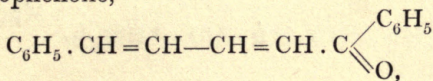
and magnesium phenyl bromide yield the ketone β-phenyl-β-styrylpropiophenone,

$$C_6H_5 . CH = CH - CH(C_6H_5) . CH_2 . CO . C_6H_5,$$

addition again occurring in the α-δ position.

Further, it has been found that certain ketones can act in both the above ways, and that the relative proportions in which $\alpha\beta$ and $\alpha\delta$ addition takes place depend upon the nature of the unsaturated compound, the number and arrangement of the hydrocarbon residues, and the character of the magnesium derivatives.

A typical case of the addition of organomagnesium compounds to unsaturated esters has been investigated by (Miss) Reynolds,[162] who has studied the interaction of Grignard's reagents with the isomeric methyl esters of cinnamylideneacetic acid, $C_6H_5-CH=CH-CH=CH-CO_2CH_3$. The formation of the following compounds is possible:—
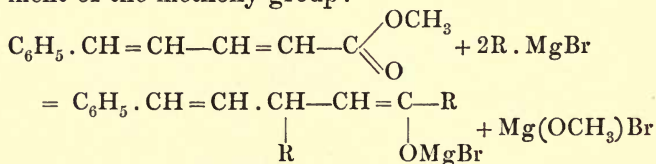
I. Tertiary alcohols, formed by replacement of the methoxy group and addition of the magnesium compound to the carbonyl group:
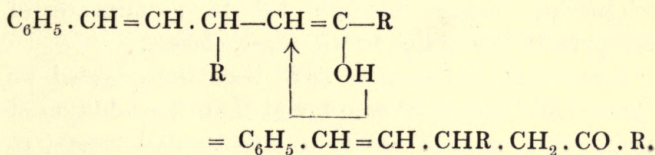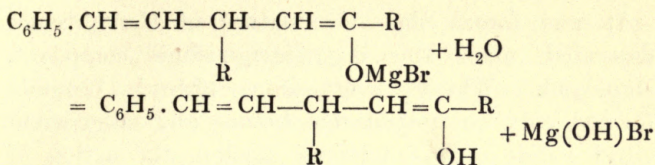
$$C_6H_5 . CH = CH - CH = CH - CR_2OH.$$
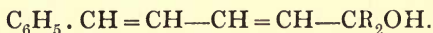
II. Unsaturated ketones,

$$C_6H_5 . CH = CH - CHR . CH_2 . C . O . R,$$
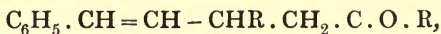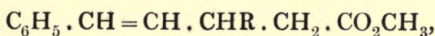
produced by $\alpha : \delta$ addition and simultaneous replacement of the methoxy group:

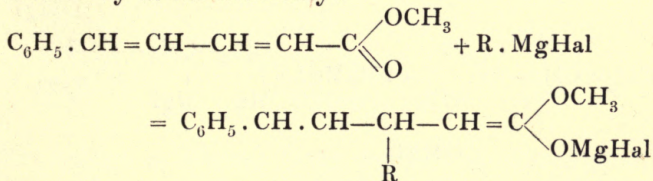$$C_6H_5 . CH = CH - CH = CH - C{\overset{\displaystyle OCH_3}{\underset{\displaystyle O}{\Big\langle}}} + 2R . MgBr$$

$$= C_6H_5 . CH = CH . \underset{\displaystyle R}{\underset{\displaystyle |}{CH}} - CH = \underset{\displaystyle OMgBr}{\underset{\displaystyle |}{C}} - R + Mg(OCH_3)Br$$

$$C_6H_5 . CH = CH—CH—CH = C—R$$
$$\underset{R}{|} \quad \underset{OMgBr}{|} \quad + H_2O$$

$$= C_6H_5 . CH = CH—CH—CH = C—R$$
$$\underset{R}{|} \quad \underset{OH}{|} \quad + Mg(OH)Br$$

$$C_6H_5 . CH = CH . CH—CH = C—R$$
$$\underset{R}{|} \quad \underset{OH}{|}$$

$$= C_6H_5 . CH = CH . CHR . CH_2 . CO . R.$$

III. Unsaturated esters of the type

$$C_6H_5 . CH = CH . CHR . CH_2 . CO_2CH_3,$$

formed by $a\delta$ addition only:

$$C_6H_5 . CH = CH—CH = CH—C{\overset{OCH_3}{\underset{O}{\big\backslash\!\!/}}} + R . MgHal$$

$$= C_6H_5 . CH . CH—CH—CH = C{\overset{OCH_3}{\underset{OMgHal}{\big\backslash\!\!/}}}$$
$$\underset{R}{|}$$

$$C_6H_5 . CH = CH . CH—CH = C{\overset{OCH_3}{\underset{OMgHal}{\big\backslash\!\!/}}} + H_2O$$
$$\underset{R}{|}$$

$$= C_6H_5 . CH = CH—CH—CH = C{\overset{OCH_3}{\underset{OH}{\big\backslash\!\!/}}} + Mg(OH)Hal$$
$$\underset{R}{|}$$

$$C_6H_5 . CH = CH . CH—CH = C{\overset{OCH_3}{\underset{OH}{\big\backslash\!\!/}}}$$
$$\underset{R}{|}$$

$$C_6H_5 . CH = CH . CHR . CH_2 . CO_2CH_3.$$
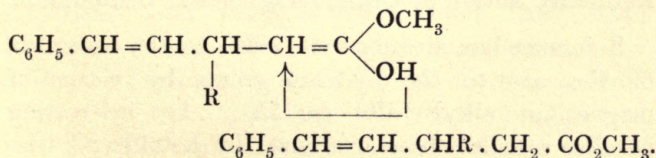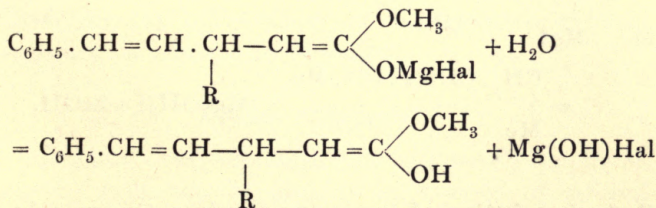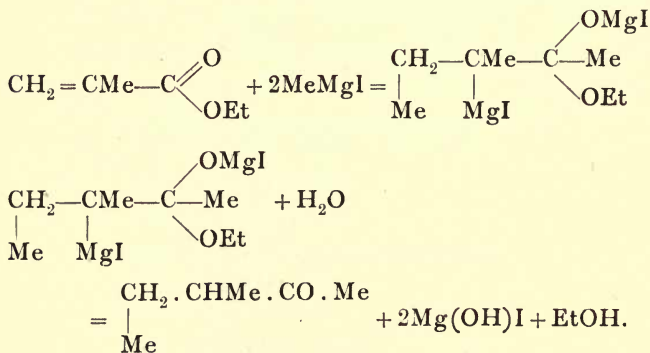
It was found that the nature of the product depended upon the organomagnesium compound employed. Whilst magnesium phenyl bromide formed only an unsaturated ketone and magnesium ethyl iodide only a tertiary alcohol, the action of magnesium benzyl bromide led to a mixture of compounds belonging to all three classes.

Somewhat similar cases have been investigated by Blaise and Courtot,[163] who found that the addition of magnesium methyl iodide to unsaturated esters, at temperatures below 0°, led to the production of ketones together with varying yields of tertiary alcohols and hydrocarbons. In this manner, ethyl a-methylacrylate yielded 3-methylpentanone (2).

$$CH_2=CMe-C{\Large\langle}^O_{OEt} + 2MeMgI = \begin{matrix} CH_2-CMe-C-Me \\ | \quad\quad | \quad\quad {\Large\langle}^{OMgI}_{OEt} \\ Me \quad MgI \end{matrix}$$

$$\begin{matrix} CH_2-CMe-C-Me \\ | \quad\quad | \quad\quad {\Large\langle}^{OMgI}_{OEt} \\ Me \quad MgI \end{matrix} + H_2O$$

$$= \begin{matrix} CH_2.CHMe.CO.Me \\ | \\ Me \end{matrix} + 2Mg(OH)I + EtOH.$$
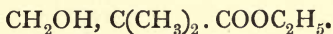
Reducing Action of Organomagnesium Compounds.

Reference has already been made to the reduction of the azo to the hydrazo group by means of magnesium alkyl salts (p. 58). An interesting parallel case has been examined by Letellier,[164] who
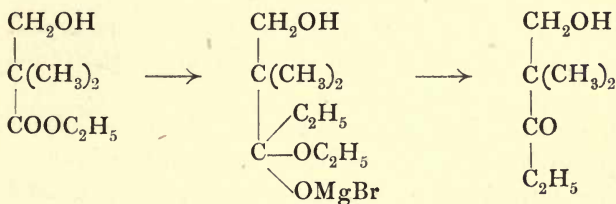
found that a certain amount of $\beta\beta$-dimethylpentane-$\alpha\gamma$-diol, $CH_2OH \cdot C(CH_3)_2 \cdot CHOH \cdot CH_2 \cdot CH_3$, was formed in addition to the tertiary alcohol, $\beta\beta$-dimethyl-γ-ethylpentane-$\alpha\gamma$-diol,

$$CH_2OH, C(CH_3)_2 \cdot C(C_2H_5)_2OH,$$
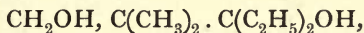
when magnesium ethyl bromide was allowed to react with ethylhydroxypivalate,

$$CH_2OH, C(CH_3)_2 \cdot COOC_2H_5.$$

The mechanism of the reduction of the former glycol is represented by the scheme:
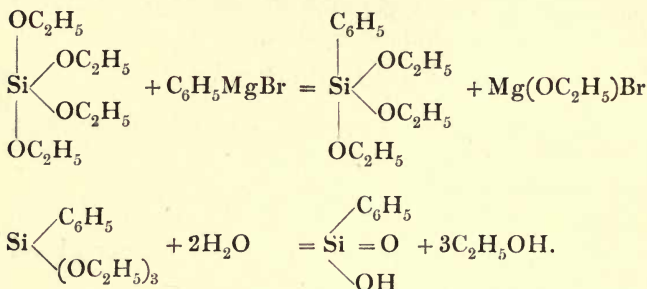

the ketone so formed being reduced by the organo-magnesium compound with the evolution of ethylene. Lowering the temperature of the reaction mixture appeared to favour the reduction.

Silicon Compounds.

Grignard's reagents have been extensively employed in the synthesis of organic compounds of silicon. Khotinsky and Seregenkoff[165] found that ethyl orthosilicate exhibited towards organomagnesium salts a behaviour similar to that of orthocarbonic ester. It was converted by magnesium phenyl bromide, for example, into ethylorthosilicobenzoate,

E

which was transformed into silicobenzoic acid by means of acids:

$$\underset{\substack{| \\ OC_2H_5}}{\overset{\substack{OC_2H_5 \\ |}}{Si}}{\overset{OC_2H_5}{\underset{OC_2H_5}{\diagup\diagdown}}} + C_6H_5MgBr = \underset{\substack{| \\ OC_2H_5}}{\overset{\substack{C_6H_5 \\ |}}{Si}}{\overset{OC_2H_5}{\underset{OC_2H_5}{\diagup\diagdown}}} + Mg(OC_2H_5)Br$$

$$Si{\overset{C_6H_5}{\underset{(OC_2H_5)_3}{\diagup\diagdown}}} + 2H_2O = Si{\overset{C_6H_5}{\underset{OH}{\diagup\diagdown}}} = O + 3C_2H_5OH.$$

Even when an excess of the reagent was employed, it appeared impossible to displace more than one ethoxy group of the ester.

A large number of derivatives of silicon have been prepared by Kipping and his co-workers,[166] who used silicon tetrachloride as starting-point, and replaced the chlorine atoms successively by alkyl or aryl radicals. The preparation of phenylbenzylethyl-propylsilicane, $Si(C_7H_9)(C_2H_5)(C_3H_7)(C_6H_5)$, may be considered as typical. Silicon tetrachloride was diluted with about three volumes of ether, the solution well cooled, and gradually treated with an ethereal solution of magnesium ethyl bromide. The main reaction may be represented by the equation:

$$SiCl_4 + MgEtBr = SiEtCl_3 + MgClBr,$$
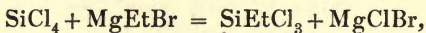
although it appears impossible to regulate the reaction in such a manner that all the silicon tetrachloride is attacked and the formation of more highly alkylated products is avoided.

When this ethylsilicon trichloride was treated with magnesium phenyl bromide, phenylethylsilicon dichloride was obtained:

$$SiEtCl_3 + PhMgBr = SiEtPhCl_2 + MgClBr.$$
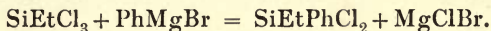
Introduction of the propyl group into this compound was effected with the aid of magnesium propyl bromide:

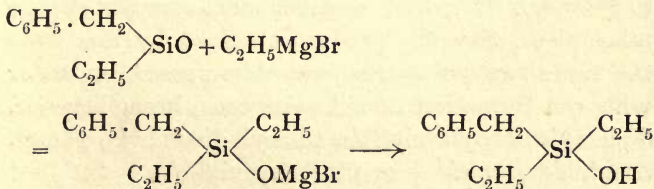$$SiEtPhCl_2 + PrMgBr = SiEtPhPrCl + MgClBr.$$
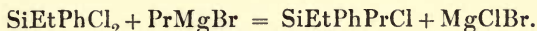
Lastly, when the siliconethylphenylpropyl chloride so obtained was treated with an ethereal solution of magnesium benzyl chloride, and the residue, after removal of the solvent, heated at about 160°, phenylbenzylethylpropylsilicane was obtained:

$$SiEtPhPrCl + MgBzCl = MgCl_2 + SiEtPhBzPrBz.$$

Compounds similar to the above have been described by Dilthey and Eduardoff[167] and by Dilthey.[168]

When dichlorides such as benzylethylsilicon dichloride are decomposed with water, silicones are obtained which react with organomagnesium salts in the same manner as ketones. Kipping and Hackford[169] found that benzylethylsilicone and magnesium ethyl bromide yielded benzyldiethylsilicol:

$$\begin{array}{c} C_6H_5.CH_2 \\ \diagdown \\ \diagup \\ C_2H_5 \end{array}\!\!SiO + C_2H_5MgBr$$

$$= \begin{array}{c} C_6H_5.CH_2 \\ \diagdown \\ \diagup \\ C_2H_5 \end{array}\!\!Si\!\!\begin{array}{c} C_2H_5 \\ \diagdown \\ OMgBr \end{array} \longrightarrow \begin{array}{c} C_6H_5CH_2 \\ \diagdown \\ \diagup \\ C_2H_5 \end{array}\!\!Si\!\!\begin{array}{c} C_2H_5 \\ \diagdown \\ OH \end{array}$$

Bygdén [170] has described similar compounds in addition to hexamethylsilicoethane, $(CH_3)_3Si . Si(CH_3)_3$, which resulted from the interaction of silicon hexachloride with magnesium methyl bromide in ethereal solution.

Martin [171] has observed that complex silicon compounds containing silicon chains, such as
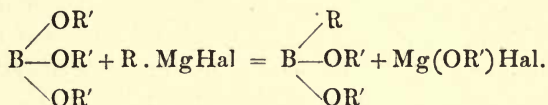
$$O{=}Si{-}OH$$
$$|$$
$$C_2H_5{-}Si{-}OH$$
$$|$$
$$HO{-}Si{-}OH$$
$$|$$
$$C_2H_5Si(OH)_2,$$
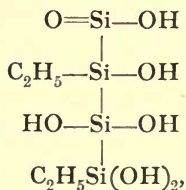
are obtained when a solution of silicon tetrachloride (1 mol.) in dry ether is brought into reaction with magnesium (2 atoms) and ethyl bromide (1 mol.), and the product decomposed by water.

Action of Grignard's Reagents on various Inorganic Substances.

The action of organomagnesium salts upon sulphur chloride has been examined by Strecker,[172] who found that this substance yielded phenyl disulphide when treated with magnesium phenyl bromide. According to Ferrario,[173] however, a rather more complex change takes place, since the product obtained by him from the same two substances was decomposed by water with the formation of chlorobenzene, bromobenzene, diphenyl, phenyl sulphide, phenyl disulphide, phenyl trisulphide, and phenyl tetrasulphide. Sulphur

dichloride and sulphur tetrachloride furnished similar products when similarly treated.

Khotinsky and Melamed[174] observed that organo-magnesium compounds react with boric esters in much the same manner as with the esters of ortho-carbonic and orthosilicic acids, only one alkoxy group being replaced by a hydrocarbon radical:

$$B{\Large\langle}\begin{array}{l}OR'\\OR'\\OR'\end{array} + R\,.\,MgHal\ =\ B{\Large\langle}\begin{array}{l}R\\OR'\\OR'\end{array} + Mg(OR')\,Hal.$$

The resulting esters of alkylated boric acids were readily hydrolysed by water to the corresponding acids. Aryl boric acids were best prepared by the action of *iso*butyl borate on aryl magnesium halides; but, on the other hand, the best yields of akyl boric acids were obtained from methyl borate.

It was also noticed that methyl borate has a methylating action on magnesium phenyl bromide, since toluene was obtained in addition to phenyl boric acid.

According to Strecker,[175] only one of the chlorine atoms of boron trichloride is replaced when the latter substance reacts with magnesium phenyl bromide. The ultimate product of the action is phenyl boric acid, resulting from the decomposition of phenylborondichloride by water.

Pfeiffer and Schnurmann[176] have prepared a series of tin alkyl compounds by the action of Grignard's reagents upon tin tetrahalides. Tin tetraethyl and tin tetraphenyl were obtained from stannic chloride

and magnesium ethyl bromide and magnesium phenyl bromide respectively :

$$SnCl_4 + 4C_6H_5MgBr = Sn(C_6H_5)_4 + 4MgBrCl,$$
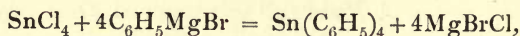
whilst magnesium benzyl chloride yielded tribenzylstannic chloride, $Sn(C_6H_5CH_2)_3Cl$.

The same authors[177] have also converted tin tetraiodide into methylstannic tri-iodide, CH_3SnI_3, and trimethylstannic iodide $(CH_3)_3SnI$, by means of magnesium methyl iodide, whilst Davies and Kipping[178] found that diethylstannic chloride, $(C_2H_5)_2SnCl_2$, was produced when stannic chloride (1 mol.) and ethyl bromide (1 mol.) reacted with magnesium in ethereal solution.[179]

In a further series of papers, Pfeiffer and Schnurmann[180] have extended their researches to a variety of inorganic chlorides. Lead chloride was found to react readily with magnesium phenyl bromide with the production of lead tetraphenyl and deposition of metallic lead :

$$2PbCl_2 + 4C_6H_5MgBr = Pb(C_6H_5)_4 + 4MgClBr + Pb.$$
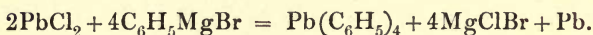
Under similar circumstances, mercuric chloride yielded mercury diphenyl, $Hg(C_6H_5)_2$, whilst mercurous chloride also readily yielded the same product, with liberation of metallic mercury.

The triphenyl derivatives of phosphorus, arsenic, and bismuth were readily obtained from the corresponding trihalides. Antimony triphenyl and tri-*p*-tolyl were also prepared from antimony trichloride, and magnesium phenyl bromide and magnesium *p*-tolyl bromide respectively.

Sachs and Kantorowicz [181] found that finely powdered arsenious oxide readily reacted with ethereal solutions of organomagnesium salts. With a cold solution of magnesium phenyl bromide it yielded diphenylarsenic oxide, $(C_6H_5)_2As \cdot O \cdot As(C_6H_5)_2$, whilst prolonged heating of the two substances resulted in the formation of triphenylarsine, $As(C_6H_5)_3$.

SECTION III.

THEORETICAL.

In what has already been written, it has been tacitly assumed that organomagnesium halides may be represented by the general formula, $R . Mg . Hal$. The use of such formulæ does not, in general, involve any inaccuracy, and has been adopted for the sake of simplicity and economy of space. Indeed, such so-called "individual" complexes have been prepared by Tschelinzeff,[182] by the interaction of magnesium and various halides in benzene solution in the presence of a trace of ether or anisole. They form white masses which contain no ether, and which exhibit all the characteristic reactions of Grignard's reagents.
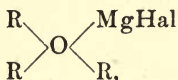
The preparation of magnesium organic salts in ethereal solution, however, does not lead to the production of "individual" compounds. Thus, when ethyl iodide reacts with magnesium in the presence of ether and the reaction-product is heated under diminished pressure in a current of dry hydrogen, the ether is not completely expelled, a portion of it being so firmly retained that it can only be partly removed even at 100° to 125°. In the residue there exists the compound,

$$C_2H_5MgI . (C_2H_5)_2O.$$
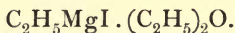
This ether was at first regarded by Grignard and Blaise as playing the part of ether of crystallisation. v. Baeyer,[183] however, proposed to formulate these substances as oxonium compounds, the oxygen atom being quadrivalent:
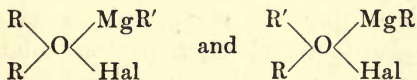
$$\begin{array}{c}R \\ \diagdown \\ R \diagup \end{array} O \begin{array}{c} \diagup MgR \\ \diagdown Hal \end{array}$$
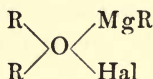
An alternative formula was proposed by Grignard:

$$\begin{array}{c}R \\ \diagdown \\ R \diagup \end{array} O \begin{array}{c} \diagup MgHal \\ \diagdown R, \end{array}$$

whilst the compounds have also been regarded in accordance with Werner's ideas and formulated:

$$\left(\begin{array}{c}R \\ \diagdown \\ R \diagup \end{array} O \ldots MgR \right) Hal$$
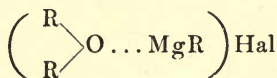
If the formula of v. Baeyer be accepted, isomerides of the type

$$\begin{array}{c}R \\ \diagdown \\ R \diagup \end{array} O \begin{array}{c} \diagup MgR' \\ \diagdown Hal \end{array} \quad \text{and} \quad \begin{array}{c}R' \\ \diagdown \\ R \diagup \end{array} O \begin{array}{c} \diagup MgR \\ \diagdown Hal \end{array}$$

appear possible. Tschelinzeff, indeed, accords preference to v. Baeyer's formula, since he claims to have established cases of isomerism of the above type in which $R = C_2H_5$, and $R' = C_3H_7$, C_4H_9, C_5H_{11} or C_6H_5. Grignard[184] maintains that the above result does not invalidate the formula proposed by him, since it may be assumed that the two additional valencies of oxygen in oxonium compounds have

not the same value as the normal valencies, so
that $R_2OR'MgHal$ is not necessarily identical with
$RR'ORMgHal$.

In general, the ether complexes are somewhat
difficult to characterise, since they are, as a rule,
uncrystallisable substances. Zerewitinoff[185] has,
however, succeeded in preparing a crystalline com-
pound,

$$C_5H_{11}\diagdown \diagup I$$
$$\hspace{2.2em}O$$
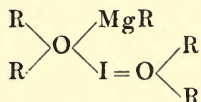$$C_5H_{11}\diagup \diagdown MgCH_3,$$
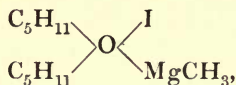
by the interaction of methyl iodide and mag-
nesium in the presence of amyl ether, and in
determining its composition by direct analysis.
Indirectly, the correctness of the formula for the
ether complexes proposed by Blaise has been verified
by Tschelinzeff,[186] who was able to show that
individual magnesium compounds combine with
ether in the presence of benzene, and that the com-
plexes so formed are soluble in this solvent. When
ether was gradually added to a suspension of an
individual magnesium compound in benzene, the
latter gradually dissolved, a perfect solution being
obtained when the ether had been added in the
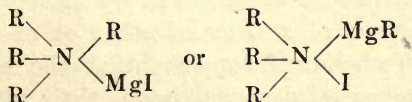proportion of one molecule for every molecule of
magnesium organic halide.

The same author [187] has measured the heat evolved
by the combination of individual magnesium com-
pounds with ether, and is led to the conclusion that
two distinct processes are involved in the preparation
of ethereal solutions of Grignard's reagents: (1) the
formation of magnesium alkyl halides, and (2) the

transformation of these substances into their ether complexes.

Subsequently Tschelinzeff[188] succeeded in showing, both by analytical and thermochemical methods, that organomagnesium compounds are capable of forming ether complexes which contain 2 molecules of ether in combination with one molecule of "individual" compound. Such a substance was actually isolated when the residue, obtained by evaporating the solvent from an ethereal solution of magnesium amyl iodide, was not too strongly heated. He proposes the general formula:

$$\begin{array}{c}
R \\
 \\
R
\end{array} \!\!\!\! {>} O {<} \begin{array}{c} MgR \\ \\ I = O \end{array} {<} \begin{array}{c} R \\ \\ R \end{array}$$

It has already been pointed out that tertiary amines, like ethers, are capable of catalysing the action of organic halides on magnesium in the presence of an inert solvent. Tschelinzeff[189] has shown that they are similarly able to unite with "individual" magnesium organic compounds, with the formation of substances which are termed *aminates*. Such substances, however, never appear to contain more than 1 molecule of the tertiary amine. Their constitution may, in all probability, be expressed by one of the two formulæ (which are analogous to those adopted for the ether complexes):

$$\begin{array}{c} R \\ R—N \\ R \end{array} {<} \begin{array}{c} R \\ \\ MgI \end{array} \qquad \text{or} \qquad \begin{array}{c} R \\ R—N \\ R \end{array} {<} \begin{array}{c} MgR \\ \\ I \end{array}$$
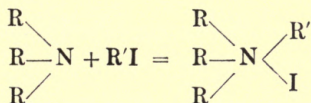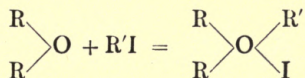
"Aminates," whilst never able to combine with a second molecule of a tertiary amine, can nevertheless unite with a molecule of ether to yield mixed ether-amine complexes. Replacement of the ether by amine, or conversely, may occur, the change proceeding in one direction or the other according to the relative stability of the resulting additive products, as shown by thermochemical measurements. In the action of ethers on "etherates" and of amines on "aminates," the compound produced is that which has the greater heat of formation. The action of ethers upon aminates is at first additive, and, with aliphatic amines, results in the formation of ether-amine complexes, since ethers cannot replace aliphatic amines. Aromatic amines may be completely displaced with the formation of dietherates. The action of an aliphatic amine on an etherate must be, at first, substitutive, but the replaced ether is added on with the formation of a mixed amine-ether complex. It is concluded from these results that addition takes place at two dissimilar positions in the molecule of the magnesium organic halide.
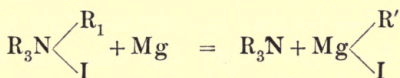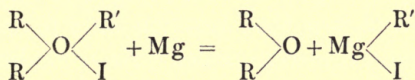
Mode of Catalytic Action of Ethers and Tertiary Amines.

Attention has already been drawn to the fact that the action of organic halides on magnesium in the presence of neutral solvents is very greatly expedited by the presence of a *trace* of ether or of a tertiary amine. Tschelinzeff supposes that the activity of these catalysers depends upon their dissociating
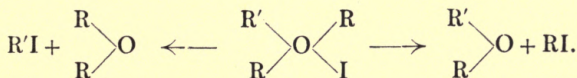
action on organic halides, which leads to the forma-
tion of oxonium or ammonium compounds:

$$\begin{array}{c} R \\ \diagdown \\ \diagup \\ R \end{array} O + R'I = \begin{array}{c} R \\ \diagdown \\ \diagup \\ R \end{array} O \begin{array}{c} R' \\ \diagdown \\ \diagup \\ I \end{array}$$

$$\begin{array}{c} R \\ \diagdown \\ R—N + R'I = R—N \\ \diagup \\ R \end{array} \begin{array}{c} R' \\ \diagdown \\ \diagup \\ I \end{array}$$

and that these compounds then react with magnesium,
with the formation of organomagnesium halides and
the regeneration of the ether or tertiary amine:

$$\begin{array}{c} R \\ \diagdown \\ \diagup \\ R \end{array} O \begin{array}{c} R' \\ \diagdown \\ \diagup \\ I \end{array} + Mg = \begin{array}{c} R \\ \diagdown \\ \diagup \\ R \end{array} O + Mg \begin{array}{c} R' \\ \diagdown \\ \diagup \\ I \end{array}$$

$$R_3N \begin{array}{c} R_1 \\ \diagdown \\ \diagup \\ I \end{array} + Mg = R_3N + Mg \begin{array}{c} R' \\ \diagdown \\ \diagup \\ I \end{array}$$

If this is actually the case, it should be possible to
find an ether the oxonium compound of which can
dissociate in two directions, with the production of two
different organomagnesium compounds:

$$R'I + \begin{array}{c} R \\ \diagdown \\ \diagup \\ R \end{array} O \longleftarrow \begin{array}{c} R' \\ \diagdown \\ \diagup \\ R \end{array} O \begin{array}{c} R \\ \diagdown \\ \diagup \\ I \end{array} \longrightarrow \begin{array}{c} R' \\ \diagdown \\ \diagup \\ R \end{array} O + RI.$$

Stadnikoff[190] has discovered such a case in the action
of n-propyl iodide and magnesium in the presence
of triphenylmethylethyl ether, $(C_6H_5)_3C . O . C_2H_5$.
When the product of this reaction was treated with
dry carbon dioxide and subsequently with water,

butyric acid and triphenylmethane were obtained. This points to a fission of the complex molecule

$$(C_6H_5)_3C \qquad MgI$$
$$\Big\rangle O \Big\langle$$
$$C_2H_5 \qquad C_3H_7$$
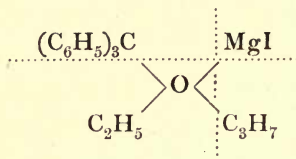
into magnesium *n*-propyl iodide on the one hand and magnesium triphenylmethyl iodide on the other. The action of carbon dioxide on the latter substance would, *a priori*, be expected to lead to the formation of triphenylmethylacetic acid, $(C_6H_5)_3C \cdot COOH$, but it has been shown that reaction only takes place in this particular direction under certain conditions.

In a second contribution on the same subject, Stadnikoff[191] has further investigated this interesting point, and has shown that the oxonium compound formed during the interaction of propyl iodide with magnesium in the presence of triphenylmethylethyl ether can be caused to dissociate into triphenylmethyl iodide and ethylpropyl ether,

$$(C_6H_5)_3C \quad I$$
$$O$$
$$C_2H_5 \qquad C_3H_7,$$
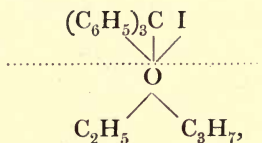
whilst, with the same ether, *iso*butyl iodide in the presence of magnesium forms an oxonium compound which decomposes with the production of triphenyl-methyl iodide and ethyl*iso*butyl ether.   Diphenyl-

methylpropyl ether and *iso*butyl iodide similarly react to yield the oxonium compound,

$$(C_6H_5)_2CH \diagdown \diagup I$$
$$O$$
$$C_3H_7 \diagup \diagdown C_4H_9,$$
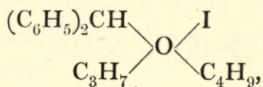
which subsequently undergoes decomposition in three ways, giving (1) diphenylmethyl iodide, $(C_6H_5)_2CHI$, and propyl*iso*butyl ether, $C_3H_7 . O . C_4H_9$; (2) *iso*-butyl iodide and diphenylmethylpropyl ether, $(C_6H_5)_2CH . O . C_3H_7$; and, probably (3) propyl iodide and diphenylmethyl*iso*butyl ether, $(C_6H_5)_2CH.O.C_4H_9$.

SECTION IV.

THE great activity of magnesium organic compounds, to which the latter owe their extended use as synthetic agents, is, under certain circumstances, very disadvantageous, since, when a substance possesses two or more points of attack for the Grignard reagent, it is frequently difficult or even impossible to limit the attack in such a manner that only one group is acted on. Thus, in the case of acid chlorides, the action of organomagnesium derivatives generally takes place in such a manner that not only is the chlorine atom replaced, but, in addition, the carbonyl group is attacked. A reagent of less general activity and of greater ease of control is thus desirable—not to replace the Grignard's reagents, but rather to act as their complement in those cases in which the latter prove themselves too energetic. Such a reagent has been found by Blaise and his co-workers in the mixed organometallic derivatives of zinc.[192]

In the formation of zinc alkyls by the interaction of zinc and alkyl iodide, the intermediate formation of substances of the type R-Zn-I has been generally assumed, although such compounds have never been analysed. Bewad[193] has attempted to bring such substances into reaction by the addition of ether—a method, however, which has still much of the

inconvenience of the preparation of zinc alkyls. Michael, on the other hand, has shown that zinc-copper couple is soluble in absolute ethereal solutions of alkyl iodides at the temperature of the water-bath, and from the couple, ethyl iodide and benzoyl chloride, has prepared propiophenone in 30 per cent. yield.
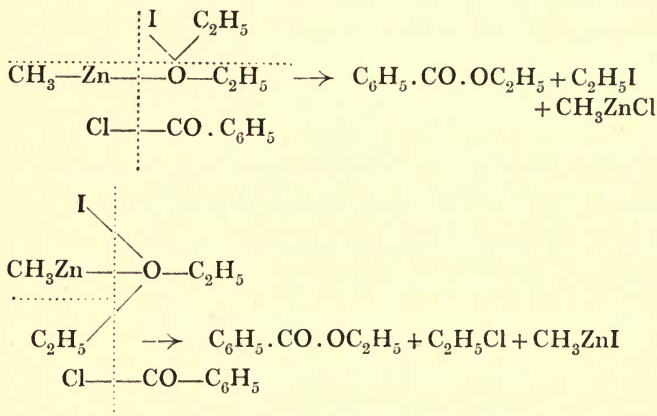
There would thus appear to be a striking analogy between the mode of formation of organometallic compounds of zinc and those of magnesium. If, however, the ethereal solution of zinc ethyl iodide is evaporated at the ordinary pressure or under a pressure of 22 mm. of hydrogen, ether and zinc ethyl are obtained. At the ordinary temperature and at a lower pressure of hydrogen a colourless mass is finally left, the analyses of which do not yield concordant results. Since, however, the presence of ether is necessary to the reaction under the experimental conditions actually adopted, it seems possible that compounds of the type

$$\begin{array}{c} C_2H_5 \diagdown \quad \diagup I \\ O \\ C_2H_5 \diagup \quad \diagdown ZnR \end{array}$$
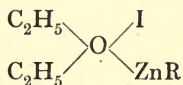
are actually formed, by which the ether is only loosely retained.

On repetition of Michael's experiment (see above), Blaise made the remarkable discovery that the activity of the organozinc derivatives is not exhausted by the addition of an equimolecular amount of benzoyl chloride, as would be expected, but that nearly five molecular proportions of the latter were required before action ceased. Among the products of the change were methane, ethyl chloride, ethyl iodide,

F

ethyl benzoate, a small quantity of acetophenone, and a brown resin. The latter substance evidently resulted from the condensation of acetophenone with loss of water, which accounted also for the evolution of methane. The formation of the other substances is explained by the scheme :

$$CH_3—Zn \begin{matrix} I & C_2H_5 \\ \diagdown \diagup \\ —O—C_2H_5 \\ \\ Cl—\!—CO.C_6H_5 \end{matrix} \longrightarrow C_6H_5.CO.OC_2H_5 + C_2H_5I + CH_3ZnCl$$

$$CH_3Zn \begin{matrix} I \diagdown \\ \diagdown \\ —\!—O—C_2H_5 \\ \diagup \\ C_2H_5 \diagup \\ Cl—\!—CO—C_6H_5 \end{matrix} \longrightarrow C_6H_5.CO.OC_2H_5 + C_2H_5Cl + CH_3ZnI$$

The mixed organometallic derivative of zinc thus liberated could then combine with a further portion of ether and again react, the final destruction of its activity being due entirely to the water formed by condensation of the acetophenone.

When, then, acid chlorides are to be employed (the most important case with zinc organic compounds), ether thus appears to be an unsuitable solvent. Blaise has shown that its place may be taken by a benzenoid hydrocarbon (particularly toluene) or by petrol, if ethyl acetate is used as catalyst. The following example may be considered as typical of the mode of preparation of the reagent :—

Zinc-copper couple (twice the weight theoretically necessary) is mixed with alkyl iodide (1 mol.), ethyl acetate ($\frac{1}{8}$ mol.), and dry toluene (double the weight of ethyl acetate used), and heated under reflux to about 100°. Reaction generally starts readily, but the commencement may be facilitated by the addition of a trace of iodine. The action then proceeds regularly, shaking being necessary occasionally. Towards the end the temperature is raised to about 110°, when, after about three-quarters of an hour, cessation of refluxing shows the completion of the change. The reaction-mixture is allowed to cool completely, an amount of toluene equal to that originally employed is added, and the solution decanted into a dry flask. It consists of an almost colourless, rather viscous liquid, which rapidly oxidises when exposed to air with separation of iodine.

The reaction can only be effected with alkyl *iodides*, which must be freed as completely as possible from the corresponding alcohol. Those containing more than four carbon atoms are best prepared by saturating the corresponding alcohol with gaseous hydrogen iodide. Toluene and ethyl acetate must be perfectly dry. The former may be desiccated by simple distillation; the latter should be thoroughly washed with saturated sodium chloride solution, dried during twenty-four hours over calcium chloride, and subsequently distilled over a fresh portion of the latter substance.

With alkyl iodides of high molecular weight it is advisable to increase the amount of ethyl acetate somewhat. With primary alkyl iodides the yield of

organometallic derivative is about 80 per cent. of the theoretical.

With secondary alkyl iodides the above method is only partly successful, since they react with benzenoid hydrocarbons in the presence of zinc, with the formation of benzene derivatives. Thus cymene was formed during the reaction of *iso*propyl iodide and zinc in the presence of toluene. If, however, petrol is used as solvent (generally the fraction of b.p. 85° to 90°), a brisk interaction occurs, and zinc alkyl iodides are formed in 60 per cent. yield. Certain amounts of ethylenic hydrocarbons and of saturated hydrocarbons containing twice as many carbon atoms as the original alkyl halide are simultaneously formed.

Tertiary alkyl iodides do not give satisfactory results.

The formation of zinc aryl iodides does not appear to take place directly under conditions which are favourable to their ready use as synthetic agents. It may, however, be readily achieved by double decomposition between magnesium aryl halides and zinc chloride. For this purpose, zinc chloride (1 mol.) is dissolved in ether (2 mols.), whereby a complex

$$(C_2H_5)_2O \underset{Zn}{\overset{Cl\quad Cl}{<\quad>}} O(C_2H_5)_2$$
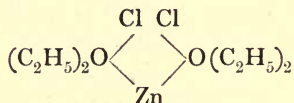
appears to be formed. This is added, drop by drop, to a solution of the requisite Grignard's reagent prepared in the ordinary manner. Toluene (5 mols. for each molecule of halide used) is then added when the zinc aryl halide is completely precipitated. It is
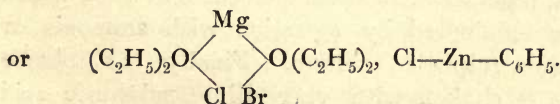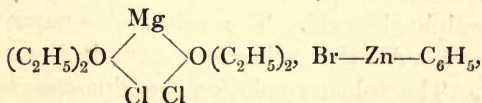
then only necessary to heat the solution under diminished pressure until all the ether is removed and the toluene begins to distil freely, when the zinc aryl halide is ready for use. The yield is about 70 per cent.

Constitution of Mixed Organometallic Derivatives of Zinc.—The action of zinc-copper couple on methyl or ethyl iodide leads to the formation of crystals, for which the formula $R.Zn.I$ has been generally assumed. The solutions prepared as described above also give an abundance of similar crystals, which, however, are so susceptible to the least trace of air or moisture that their isolation in the pure state is almost impossible. By allowing zinc ethyl iodide to react with ethyl oxalate, a crystalline compound has been obtained, analyses of which agree well with the formula:

$$C_2H_5O.CO.C(C_2H_5)_2.O.ZnI,$$
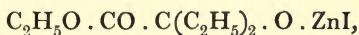
from which the formula C_2H_5ZnI appears probable for zinc ethyl iodide.

Similarly, the precipitate obtained by allowing zinc chloride to react with phenyl magnesium bromide appears to possess the composition indicated by the formula:

$$(C_2H_5)_2O \diagup \!\!\!\! \overset{\textstyle Mg}{\underset{\textstyle Cl\ Cl}{}} \!\!\!\! \diagdown O(C_2H_5)_2,\ Br\!\!-\!\!Zn\!\!-\!\!C_6H_5,$$

or

$$(C_2H_5)_2O \diagup \!\!\!\! \overset{\textstyle Mg}{\underset{\textstyle Cl\ Br}{}} \!\!\!\! \diagdown O(C_2H_5)_2,\ Cl\!\!-\!\!Zn\!\!-\!\!C_6H_5.$$

Mode of employment of Mixed Organozinc Compounds. — These compounds have been chiefly employed in conjunction with acid chlorides of varying types, and with compounds containing loosely held halogen atoms. The acid chlorides should be purified by distillation. If this is impossible, they should be prepared preferably by means of thionyl chloride, since excess of the latter may be readily removed by gentle heating under diminished pressure.

For a given quantity of acid chloride, an excess of 25 to 33 per cent. of the calculated quantity of alkyl zinc iodide should be employed in the case of primary alkyl iodides; with secondary alkyl iodides double the calculated quantity may be employed, whilst with zinc aryl halides an excess of 50 per cent. is generally sufficient.

The acid chloride, dissolved in toluene, is added drop by drop with constant shaking to the solution of the reagent, the temperature being maintained at about 0°. Reaction occurs readily. The temperature is then allowed to rise somewhat, and as soon as all odour of acid chloride has disappeared, the solution is again cooled and decomposed by the addition of successive small quantities of water and a little dilute sulphuric acid. The solution separates into two layers. All the iodine is present in the aqueous portion. The toluene solution contains the required product, together with small quantities of zinc, which may be eliminated by agitation with ammonia or ammonium sulphate solution. Finally, the toluene solution is shaken with very dilute sulphuric acid

and then with a solution containing potassium hydrogen carbonate and sodium thiosulphate, after which it is dried over sodium sulphate.

In general, organozinc compounds do not react in the cold with the halogen, ketonic, carbalkoxy, ethylenic, or alkoxy groups, and herein lies their chief interest. They are capable, however, of reacting with halogen atoms attached to a carbon atom to which an oxygen atom is also united, and with other mobile halogen atoms.[194]

Normal Action on Acid Chlorides.—The normal action between an acid chloride and a zinc organo-salt results in the formation of a ketone:

$$R . CO . Cl + I . ZnR' = R . CO . R' + ZnICl.$$
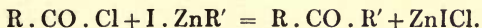
The yields are generally excellent (75 to 90 per cent.), and the products frequently pure after one distillation. A small quantity of the ethyl ester derived from the acid chloride employed is sometimes present. This can often be removed by treatment of the product with potassium hydroxide, or by formation of a solid derivative of the ketone (*e.g.* the semicarbazone), and subsequent decomposition of the latter.

Formation of Tertiary Alcohols from Acid Chlorides.—Acid chlorides or esters are readily transformable into tertiary alcohols by the action of cold solutions of organozinc salts when an electronegative group or atom is contained in the molecule in the immediate neighbourhood of the —COCl or —COOAlk group. Thus, ethyl oxalate, in which one carbethoxy group accentuates the negative

character of the other, is quantitatively transformed into the ethyl ester of a dialkylglycollic acid:

$$
\begin{array}{ccc}
\text{COOC}_2\text{H}_5 & & \text{CR}_2(\text{OH}) \\
| & \longrightarrow & | \\
\text{COOC}_2\text{H}_5 & & \text{COOC}_2\text{H}_5
\end{array}
$$

whilst ethoxyoxalyl chloride, COOEt.COCl, undergoes a similar change, in which, however, the tertiary alcohol at first produced is esterified by the action of a further portion of the acid chloride:
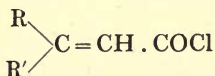
$$
\begin{array}{ccccc}
\text{COOC}_2\text{H}_5 & & \text{CO.OC}_2\text{H}_5 & & \text{COOC}_2\text{H}_5 \\
| & \longrightarrow & | & \longrightarrow & | \\
\text{COCl} & & \text{R}_2\text{:C—OZnI} & & \text{R}_2.\text{C.O.CO.CO}_2\text{C}_2\text{H}_5.
\end{array}
$$
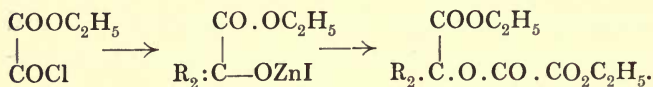
Similarly, chloroacetyl chloride and ethyl zinc iodide give, as main product, the chloroacetic ester of chloromethyldiethylcarbinol:

$$
\text{CH}_2\text{Cl.C(Et)}_2.\text{O.CO.CH}_2\text{Cl}.
$$
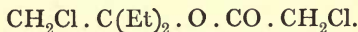
Also, the chlorides of $\alpha\beta$ unsaturated acids yield mainly ketones together with small quantities of the ester derived from the tertiary alcohol:[195]

$$
\text{R.CH} = \text{CH.COCl}
$$
$$
\longrightarrow \text{R.CH} = \text{CH.C(R')}_2.\text{O.CO.CH} = \text{CH.R}
$$
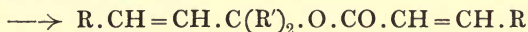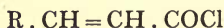
but, as the electronegative influence of the ethylenic linking is lessened by substitution the amount of ketone formed increases, so that the latter is practically the only compound obtained from acid chlorides of the types:
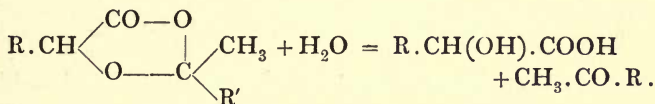
$$
\begin{array}{ccc}
\text{R} & & \text{R} \\
\diagdown & & \diagdown \\
\quad \text{C} = \text{CH.COCl} & \text{and} & \quad \text{C} = \text{CR}_1.\text{COCl}. \\
\diagup & & \diagup \\
\text{R}' & & \text{R}'
\end{array}
$$
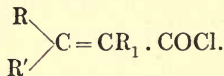
The action of organic zinc halides on the chlorides of α-acetoxy acids is of particular interest.[196] Apparently the carbonyl group of the acetyl radical is attacked preferably to the chlorine atom of the acid chloride. Cyclic acetals are thus obtained:
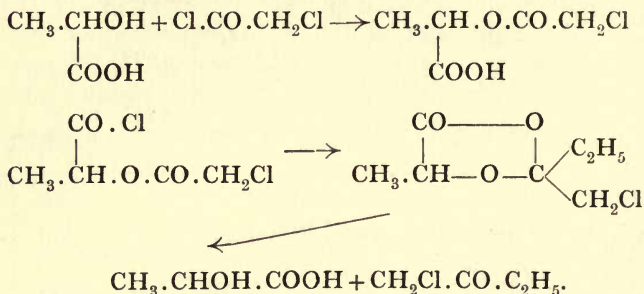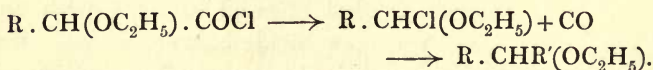
$$R.CH\begin{cases}COCl \\ O-CO-CH_3\end{cases} \longrightarrow R.CH\begin{cases}CO-Cl \\ O-C\begin{cases}OZnI \\ CH_3 \\ R'\end{cases}\end{cases}$$

$$\longrightarrow R.CH.\begin{cases}CO-O \\ O-C\begin{cases}CH_3 \\ R'\end{cases}\end{cases}$$
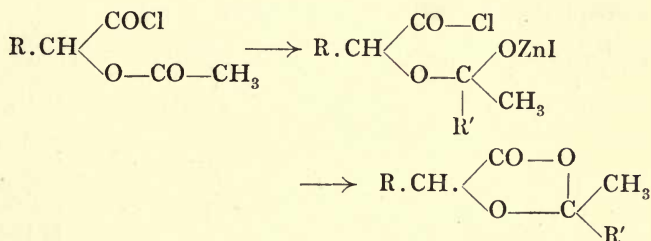
which, on hydrolysis, yield ketones:

$$R.CH\begin{cases}CO-O \\ O-C\begin{cases}CH_3 \\ R'\end{cases}\end{cases} + H_2O = R.CH(OH).COOH + CH_3.CO.R.$$

One group of the ketone is thus derived from the acetyl radical, the other from the organozinc derivative. A means is thus provided of obtaining ketones from those acid chlorides which, with zinc alkyl halides, normally yield tertiary alcohols.[197] The acid chloride is first allowed to react with an α-hydroxy acid, the new acid converted into its chloride, which is then subjected to the action of the requisite organozinc derivative. The cyclic acetal so obtained yields, on hydrolysis, the required ketone. The preparation of chloromethylethylketone may be considered as typical. Chloroacetyl chloride and zinc ethyl iodide yield mainly the chloroacetic ester of chloromethyldiethylcarbinol (see above). If,

however, chloroacetyl chloride is allowed to react
with lactic acid, α-chloroacetoxypropionic acid is
formed, the chloride of which reacts with ethyl zinc
iodide to yield the corresponding *cyclo*acetal. This,
when hydrolysed by acid, is resolved into chloro-
methylethyl ketone and lactic acid:

$$CH_3.CHOH + Cl.CO.CH_2Cl \longrightarrow CH_3.CH.O.CO.CH_2Cl$$
$$\quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad | $$
$$\quad\quad COOH \quad\quad\quad\quad\quad\quad\quad\quad\quad COOH$$

$$\begin{array}{c} CO.Cl \\ | \\ CH_3.CH.O.CO.CH_2Cl \end{array} \longrightarrow \begin{array}{c} CO\!-\!\!-\!\!-\!\!-O \\ |\quad\quad\quad| \!\diagup^{C_2H_5} \\ CH_3.CH\!-\!O\!-\!C\diagdown_{CH_2Cl} \end{array}$$

$$\longleftarrow$$

$$CH_3.CHOH.COOH + CH_2Cl.CO.C_2H_5.$$

In certain cases, catalytic decomposition of acid
chlorides may be occasioned by the action of zinc
organic salts—especially in the case of α-alkoxy
acid chlorides.[198] Under these circumstances carbon
monoxide is evolved, and the residual α-chloroether
then reacts normally with replacement of the halogen
atom:

$$R.CH(OC_2H_5).COCl \longrightarrow R.CHCl(OC_2H_5) + CO$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \longrightarrow R.CHR'(OC_2H_5).$$

Reducing action of mixed organozinc derivatives
has only been observed in the case of sulphonic
chlorides. Thus, benzene sulphonic chloride and
ethyl zinc iodide give a small quantity of the
sulphone, but the main product of the reaction is
found in the form of zinc benzene sulphinate.

Mixed organozinc compounds readily react with substances containing mobile halogen atoms—such compounds generally containing the halogen atom united to carbon, which is itself attached to oxygen. Such compounds comprise α-chloroethers, acid chlorides of the succinic and glutaric series, ethyl chloroethoxy-acetate, $CHCl(OC_2H_5) . COOC_2H_5$, and ethyl dichloro-ethoxyacetate, $CCl_2(OC_2H_5) . COOC_2H_5$. The use of α-chloroethers possesses no feature of special interest, since these substances react equally well with Grignard's reagents. Acid chlorides of the succinic series yield, practically entirely, γ-lactones, whilst those of the glutaric series give a mixture of δ-lactone and δ-keto acid.[199] Ethyl chloroethoxy-acetate [200] reacts very readily with alkyl zinc iodides, giving excellent yields of ethyl alkylethoxyacetate,

$$CHCl(OEt) . COOEt \longrightarrow R . CH(OEt) . COOEt,$$
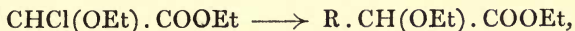
whilst similar compounds are also readily obtained from ethyl dichloroethoxyacetate,[201]

$$CCl_2(OC_2H_5) . COOC_2H_5 \longrightarrow CR_2(OC_2H_5) . COOC_2H_5.$$
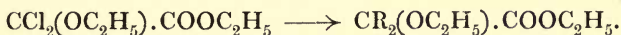
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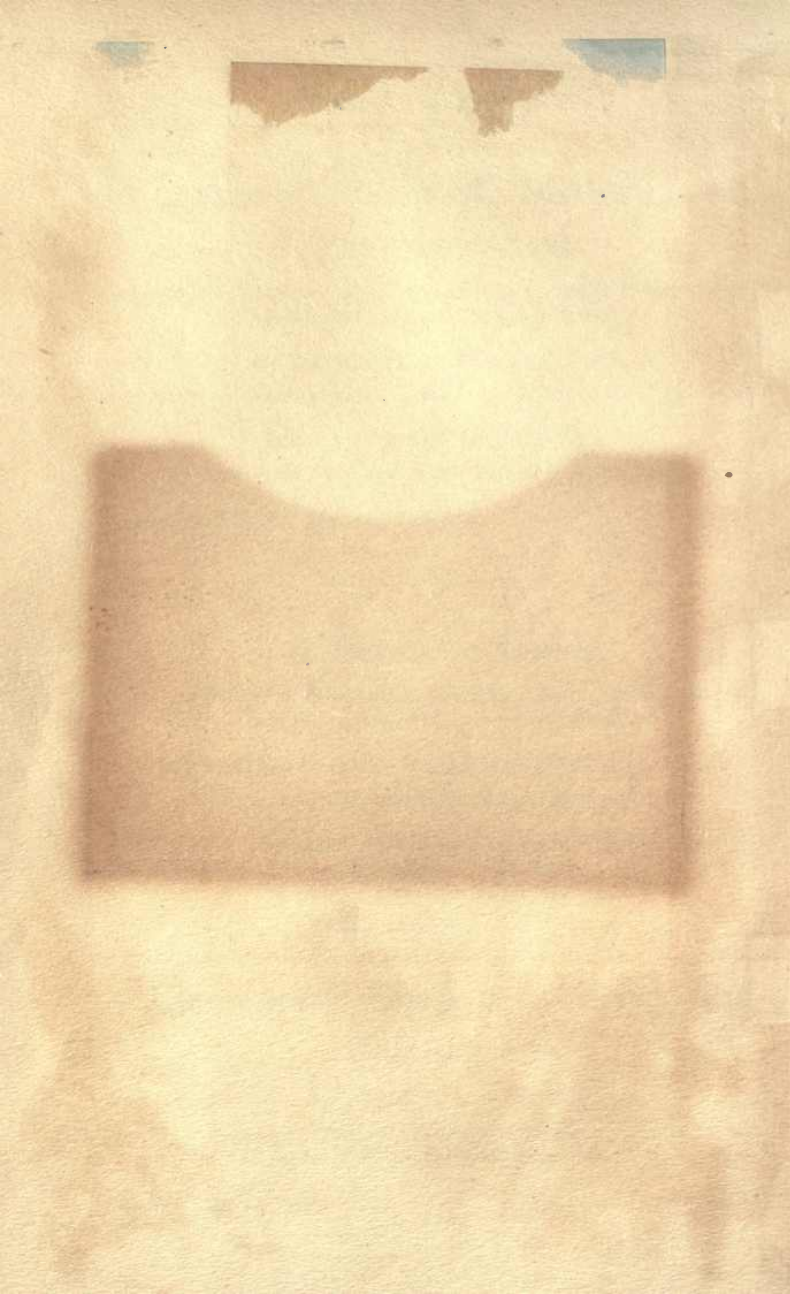
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